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Vol. 20, No. 1 January 1938

CONTENTS

RP	TITLE AND AUTHOR	Page
1059.	Water tolerances of mixtures of gasoline with ethyl alcohol. Oscar C. Bridgeman and Elizabeth W. Aldrich.....[Price 5c]	1
1060.	Critical solution temperatures of mixtures of gasoline, *n*-propyl alcohol, and water. Elizabeth W. Aldrich.....[Price 5c]	9
1061.	Interference measurements in the first spectra of neon, argon, and krypton between 4812 and 3319 A. Curtis J. Humphreys [Price 10c]	17
1062.	Infrared spectra of iron, titanium, and carbon. Carl C. Kiess [Price 5c]	33
1063.	Consistency of eight types of vitreous enamel frits at and near firing temperatures. William N. Harrison, Robert E. Stephens, and Stephen M. Shelton.....[Price 10c]	39
1064.	Some "soft" glazes of low thermal expansion. R. F. Geller, E. N. Bunting, and A. S. Creamer.....[Price 5c]	57
1065.	Strength, water absorption, and resistance to freezing and thawing of sand-lime brick. John W. McBurney and Allan R. Eberle [Price 5c]	67
1066.	Approximate glass content of commercial portland cement clinker. William Lerch.....[Price 5c]	77
1067.	A laboratory extraction apparatus and its use in separating a lubricating-oil fraction with acetic acid. Sylvester T. Schicktanz [Price 5c]	83
1068.	Volumetric determination of alpha-, beta-, and gamma-cellulose in pulps and in papers containing sizing, filler, and other materials. Herbert F. Launer.....[Price 5c]	87

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RESEARCH PAPER RP1059

Part of Journal of Research of the National Bureau of Standards, Volume 20, January 1938

WATER TOLERANCES OF MIXTURES OF GASOLINE WITH ETHYL ALCOHOL

By Oscar C. Bridgeman and Elizabeth W. Aldrich

ABSTRACT

Equations, based on 23 different gasolines, have been developed for calculating the water tolerance of any mixture of gasoline with ethyl alcohol from critical-solution-temperature measurements on a few mixtures with the particular gasoline. Conversely, it is also possible to compute critical solution temperatures of mixtures of known composition. The average deviation between observed and calculated critical solution temperatures of the 23 gasolines studied was 1.4° C and the corresponding average difference between observed and calculated water tolerances was 0.005 percent of the total mixture.

CONTENTS

	Page
I. Introduction	1
II. Analytical treatment of data	1
III. Summary	7

I. INTRODUCTION

One of the major problems in connection with the use of mixtures of gasoline and ethyl alcohol as motor fuels involves the small water tolerances of such fuels without separation into two layers. In previous papers,[1] data were presented on the critical solution temperatures of mixtures, in various proportions, of 23 different gasolines with ethyl alcohol containing various percentages of water. From these data, it is easily possible to obtain the water tolerance of any of these gasolines at any given temperature within the range investigated. Analysis of the water-tolerance values indicated certain similarities in the trend of water tolerance with composition of the mixtures when comparing the results with different gasolines. This suggested the possibility of deriving a general empirical equation for the water tolerance of mixtures of gasoline and ethyl alcohol, and of assigning to any gasoline a characteristic constant which would be indicative of the water tolerance of all mixtures of this gasoline with ethyl alcohol. The derivation of such an equation and the evaluation of the characteristic constants for the various gasolines are outlined in the present paper.

II. ANALYTICAL TREATMENT OF DATA

The first step in the procedure of analyzing the experimental data consisted in the computation of the water content of each mixture

[1] Oscar C. Bridgeman and Dale Querfeld. *Critical solution temperatures of mixtures of gasoline, ethyl alcohol, and water*, BS J. Research **10**, 693 (1933) RP560; *The effect of gasoline volatility on the miscibility with ethyl alcohol*, BS J. Research **10**, 841 (1933) RP571.

of gasoline and ethyl alcohol investigated. This was accomplished simply by multiplying the volume percentage of water at 60° F in the aqueous alcohol solution employed by the volume percentage of aqueous alcohol solution at 60° F in the mixture with gasoline. The resulting value, expressed as percentage of the total mixture, was designated as the water tolerance of the mixture at the critical solution temperature. On plotting the logarithm of the water tolerance against the reciprocal of the critical solution temperature (absolute) for any given percentage of any one of the gasolines mixed with ethyl alcohol, it was found that a straight line could be put through the plotted points within experimental error. Accordingly,

$$\log S = a - b/T \tag{1}$$

where

S = volume percentage water in mixture at 60° F,
T = temperature in degrees centigrade absolute, and
a and b = constants characteristic of the percentage of gasoline in the mixture and of the particular gasoline employed.

Examples of the linearity of the data are shown in figure 1 for four different percentages of gasoline 2 in mixtures with ethyl alcohol.

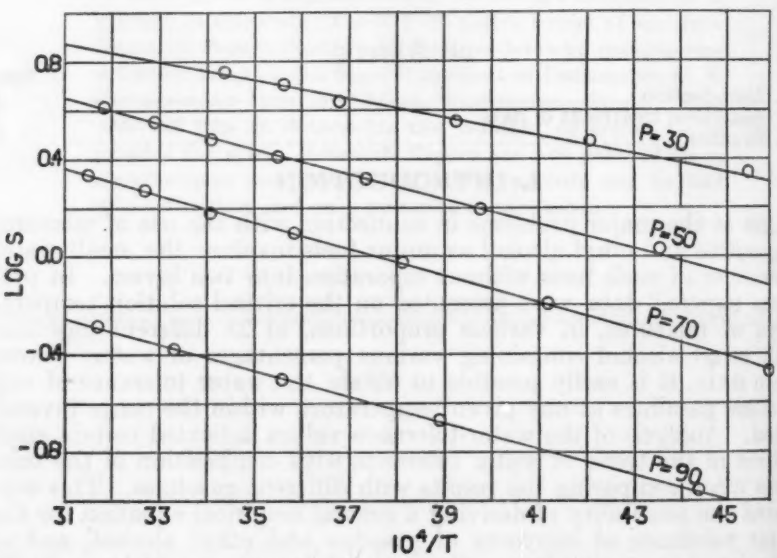

FIGURE 1.—*Log S as a function of temperature for four different percentages of gasoline 2 in mixtures with ethyl alcohol.*

Equations of the type of eq 1 were used to evaluate the parameters a and b for all of the mixtures studied. For any constant percentage P of gasoline in the mixture, it was observed that a plot of all of the b values against the corresponding a values gave a single straight line for all of the gasolines. Different lines were obtained for each value of P, although the slopes were equal within experimental error. Therefore

$$a = m + nb \tag{2}$$

where

$m=f_1(P)$ and
$n=1/410$.

Thus eq 2 becomes

$$a=f_1(P)+b/410 \tag{3}$$

It was found that $f_1(P)$ could be represented by eq 4,

$$f_1(P)=-1.177+1.273 \log (100-P) \tag{4}$$

where P is the volume percentage of gasoline in the mixture.

It follows from eq 3 that the various parallel lines obtained when a is plotted against b may be made to coincide, if the appropriate

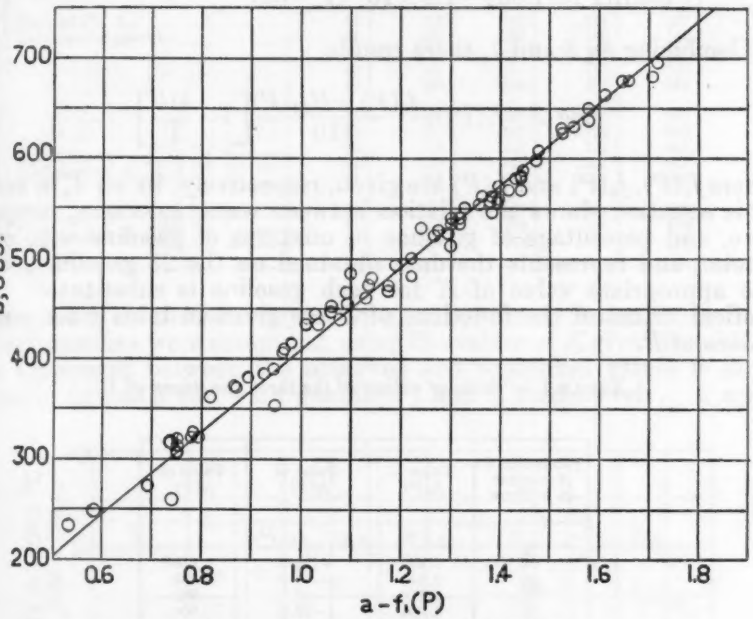

FIGURE 2.—*Comparison of b of equation 1 with b/410 from equation 3.*

value of $f_1(P)$ is subtracted from a, and the resulting values plotted against b. A plot of this nature is shown in figure 2, which indicates the agreement with eq 4.

Combining eq 1 and 3 to eliminate a, there results

$$\log S=f_1(P)+\frac{b}{410}\left[1-\frac{410}{T}\right] \tag{5}$$

In this equation, b depends upon the value of P as well as upon the characteristics of the particular gasoline being considered. The next step in the analysis, therefore, is to evaluate b as a function of P. It was observed that when the values of b for all of the gasolines at any given value of P were plotted against the values of b for $P=50$, a straight line was obtained. Thus

$$b_P=c+db_{50} \tag{6}$$

Different lines were obtained for each value of P, so that the parameters c and d are both functions of P. Since b_{50} is a constant for each gasoline, it may be designated by the symbol K and called the characteristic constant as regards water tolerance in mixtures with ethyl alcohol. Accordingly, eq 6 may be written

$$b_P = f_2(P) + Kf_3(P) \tag{7}$$

It was found that the c and d values could be represented satisfactorily by means of the following equations:

$$c = f_2(P) = -188.3 + 7.64P - 0.119P^2 + 0.00083P^3, \text{ and} \tag{8}$$
$$d = f_3(P) = 1.004 - 1.8 \times 10^{-4}(P - 55)^2 \tag{9}$$

Combining eq 5 and 7, there results

$$\log S = f_1(P) + \frac{f_2(P) + Kf_3(P)}{410}\left[1 - \frac{410}{T}\right] \tag{10}$$

where $f_1(P)$, $f_2(P)$ and $f_3(P)$ are given, respectively, by eq 4, 8, and 9. This equation shows the relation between water tolerance, temperature, and percentage of gasoline in mixtures of gasoline with ethyl alcohol and represents the data obtained on the 23 gasolines, when the appropriate value of K for each gasoline is substituted. Numerical values of the functions of P are given in table 1 for several values of P.

TABLE 1.—*Table of values of the three functions of P*

Percentage P of gasoline in mixture	Value of $f_1(P)$	Value of $f_2(P)$	Value of $f_3(P)$
%			
10	1.310	−123.0	0.639
20	1.246	−76.5	.783
30	1.172	−43.8	.892
40	1.086	−20.0	.964
50	0.986	0.0	1.000
60	.862	21.0	1.000
70	.703	48.1	0.964
80	.479	86.3	.892
90	.096	140.5	.783
95	−.287	175.1	.716

It follows from eq 10 that a single measurement of the critical solution temperature of a mixture of known composition is sufficient in principle for determining the value of the characteristic constant K for each gasoline. Accordingly, each observation on the 23 gasolines can be used to compute a value of K and this was done in order to obtain an average value for each of these gasolines. The average values of K together with identification data on the gasolines are shown in table 2. The last column in this table gives the average deviation of individual values of K from the average value of K. It is seen that the values of K vary from 421 to 669, an average commercial gasoline having a value of about 550.

TABLE 2.—*Identification data and values of K for 23 gasolines*

Fuel	Source	Temperature at stated percentages evaporated, °C			Specific gravity 60°/60°	Value of K	Average deviation of K
		10%	50%	90%			
1	Pennsylvania	76	135	199	0.738	669	14
2	Roumania	70	106	152	.734	505	9
3	California	66	108	154	.730	521	8
4	Oklahoma	72	124	194	.740	603	8
5	California	58	110	156	.732	512	8
6	East Texas	58	110	162	.723	535	9
7	100% cracked	54	126	188	.754	473	12
8	100% cracked	69	142	194	.773	518	11
9	Topped No. 1	69	107	153	.720	546	7
10	Topped No. 7	53	96	150	.722	421	9
11	Topped No. 8	60	102	153	.734	427	9
12	Commercial gasoline	61	130	180	.742	544	8
13	do	58	123	181	.742	532	10
14	do	68	127	175	.743	537	4
15	do	69	136	186	.752	562	7
16	do	65	124	174	.741	531	7
17	do	66	131	187	.752	540	9
18	10% Natural gasoline *A* 90% No. 1	64	128	197	.731	641	10
19	20% Natural gasoline *A* 80% No. 1	55	119	196	.721	607	13
20	30% Natural gasoline *A* 70% No. 1	42	104	192	.707	568	9
21	10% Natural gasoline *B* 90% No. 1	69	128	197	.736	649	8
22	20% Natural gasoline *B* 80% No. 1	61	120	195	.727	620	7
23	30% Natural gasoline *B* 70% No. 1	57	111	193	.719	571	8

As a check on the accuracy of eq 10, all of the critical solution data on each gasoline were computed, using the values of K given in table 2. The agreement between the observed and computed values is illustrated in figures 3 and 4 for gasolines 1 and 2, respectively. A summary of the deviations for all of the gasolines is given in table 3. The grand average deviation is 1.4° C (2.6° F). The deviations are given on a temperature basis, since this greatly magnifies the differences between observed and computed values, for an extremely small difference in water tolerance may correspond to several degrees difference in critical solution temperature. On the average, a temperature deviation of 1.4° C corresponds to a deviation of approximately 0.005 percent in water content and to a difference of about 10 units in the value of K.

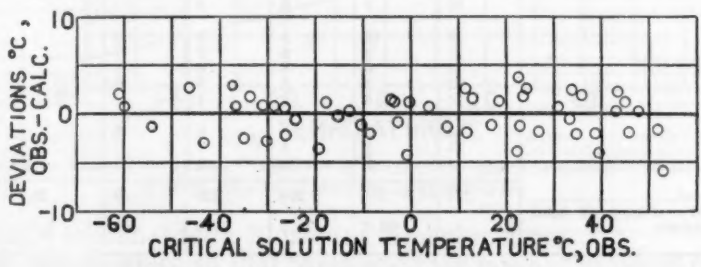

FIGURE 3.—*Comparison of values calculated from equation 10 with observed values of critical solution temperatures of mixtures of gasoline 1 with ethyl alcohol.*

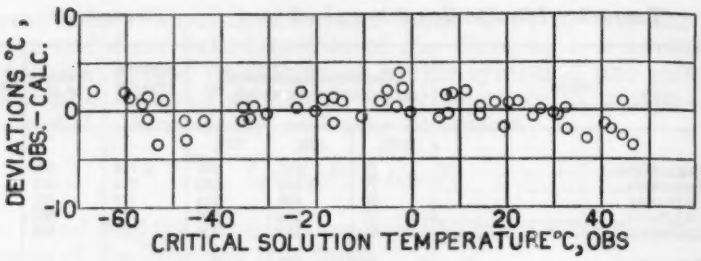

FIGURE 4.—*Comparison of values calculated from equation 10 with observed values of critical solution temperatures of mixtures of gasoline 2 with ethyl alcohol.*

TABLE 3.—*Deviations between observed and calculated critical solution temperatures*

Fuel	Total number of temperatures measured	Number of points for stated ranges of deviations in °C (without regard to sign)					
		0.0 to 1.0	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0	>4.9
1	55	12	17	14	6	3	3
2	53	22	19	9	2	1	
3	54	28	13	11	1	1	
4	54	26	18	8	2		
5	48	19	13	11	2	2	1
6	50	26	11	8	2	1	2
7	49	12	8	10	9	7	3
8	49	17	10	13	7	1	1
9	50	21	18	9	0	2	
10	46	16	16	5	4	3	2
11	46	14	18	6	6	0	2
12	15	6	7	2			
13	15	4	6	5			
14	15	12	2	1			
15	15	7	6	2			
16	15	10	3	1	0	1	
17	15	3	8	3	1		
18	13	6	6	0	1		
19	13	1	8	2	2		
20	14	6	6	1	1		
21	13	5	7	0	1		
22	14	7	5	1	1		
23	14	7	5	1	1		
Total	725	287	230	123	49	22	14
Percentage of total points		39.6	31.7	17.0	6.8	3.0	1.9

Average deviation ---------- 1.4° C (2.6° F)

The major interest at present is in 5- and 10-percent alcohol mixtures ($P=95$ and 90), and for these mixtures 10 becomes

$$P=95 \log S=-0.287+\frac{175.1+0.716\,K}{410}\left[1-\frac{410}{T}\right] \tag{11}$$

$$P=90 \log S=0.096+\frac{140.5+0.783\,K}{410}\left[1-\frac{410}{T}\right]$$

Considering an average gasoline for which $K=550$, and simplifying, there results

$$P=95 \log S=-0.287+1.388\left[1-\frac{410}{T}\right]$$

$$P=90 \log S= \quad 0.096+1.393\left[1-\frac{410}{T}\right] \tag{12}$$

Graphical representation of eq 12 is shown in figure 5. It is seen that the water tolerance for a 5-percent alcohol mixture is less than half

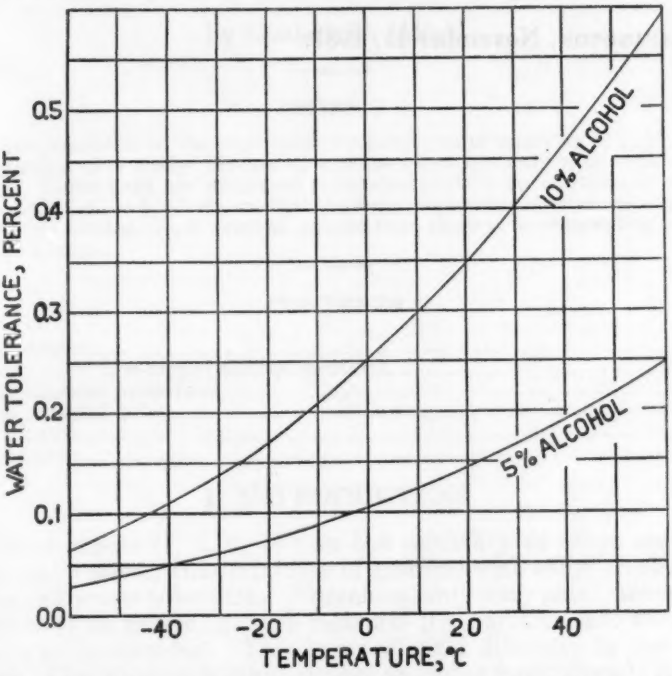

FIGURE 5.—*Water tolerances of mixtures of an average gasoline with 5 and 10 percent of ethyl alcohol at various temperatures.*

the water tolerance for a 10-percent alcohol mixture.

The data on which eq 10 is based cover the range of values of P from 10 to 90, so that the calculation for $P=95$ is an extrapolation from the observed data. However, since these calculations were made some additional data on three gasolines included measurements at $P=95$ and indicated that the equation is applicable to this percentage.

III. SUMMARY

An analysis of data previously presented, on the solubility of water in mixtures of ethyl alcohol with 23 different gasolines, indicated that it was possible to correlate the results by means of a general empirical equation. This equation contains one constant characteristic of the particular gasoline under consideration, and values of the

characteristic constants for the 23 gasolines are given. Evidence is presented regarding the agreement of the equation with the observed data, the difference between the observed and computed critical solution temperatures being 1.4° C, and the difference between the observed and computed water tolerances being about 0.005 percent of the total mixture. Since the characteristic constant may be evaluated from a few solubility experiments with any particular gasoline, the equation can be used with confidence to compute the water tolerances at other temperatures or with other mixtures.

WASHINGTON, November 11, 1937.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1060

Part of Journal of Research of the National Bureau of Standards, Volume 20, January 1938

CRITICAL SOLUTION TEMPERATURES OF MIXTURES OF GASOLINE, *n*-PROPYL ALCOHOL, AND WATER

By Elizabeth W. Aldrich

ABSTRACT

Data are presented on the separation temperatures of mixtures of 5, 10, 15, 20, and 25 percent of *n*-propyl alcohol of various water contents with each of three gasolines. These data are compared with similar data on mixtures of gasoline with ethyl alcohol, and it is shown that the water tolerances of mixtures of gasoline with *n*-propyl alcohol are, in general, greater than those of corresponding mixtures with ethyl alcohol.

CONTENTS

		Page
I.	Introduction	9
II.	Preparation of *n*-propyl alcohol solutions	9
III.	Experimental procedure	10
IV.	Experimental data	12
V.	Conclusion	16
VI.	References	16

I. INTRODUCTION

Previous papers [1, 2, 3, 4] [1] on the solubility of ethyl alcohol in gasoline have shown that mixtures of gasoline with ethyl alcohol have only a small water tolerance. Therefore, only very small percentages of water may be present in such mixtures if separation into two liquid phases is to be avoided. This is a technical difficulty in the use of mixtures of gasoline with ethyl alcohol as motor fuels, since it is necessary to use alcohol almost free from water in preparing the blend and to protect the mixed fuel from water or to add a blending agent to increase the water tolerance.

Since the solubility of methyl alcohol solutions in gasoline is less than that of ethyl alcohol solutions containing the same amount of water, it seemed probable that the solubility of the aqueous aliphatic alcohols in gasoline might increase with molecular weight. Therefore, an investigation was undertaken of the solubility of aqueous solutions of some of the higher aliphatic alcohols. The present paper deals with the solubility in gasolines of *n*-propyl alcohol containing various amounts of water in gasolines as indicated by the temperature of separation into two phases in solutions of known compositions.

II. PREPARATION OF *n*-PROPYL ALCOHOL SOLUTIONS

The *n*-propyl alcohol used in these experiments was a commercial refined product and was used without further purification. The

[1] Figures in brackets here and elsewhere in the text correspond to the numbered references at the end of this paper.

density of the alcohol was 0.79668 at 30° C and its boiling range was from 96.2 to 97.2° C. The comparatively narrow boiling range and the density, which corresponds to an aqueous solution containing 99.67 weight percent of *n*-propyl alcohol, indicate that the alcohol contained only a small amount of impurities.

Treatment of the commercial product with calcium oxide reduced the density at 30° C to 0.79605, which corresponds to an aqueous solution of *n*-propyl alcohol containing 99.91 weight percent of alcohol, and also reduced the boiling range, which became 97.2 to 97.4° C. These changes in properties on drying indicated that practically all of the impurity was water. For the present work, it was assumed that no other impurity was contained in the alcohol in sufficient quantities to affect the densities of its aqueous solutions, and the compositions of the *n*-propyl alcohol solutions used were calculated from density determinations.

Eight *n*-propyl alcohol solutions containing approximately 1 to 8 volume percent of water were prepared. The density at 30° C of each of these was determined by use of calibrated picnometers of the Osborne [5] type of approximately 21-ml capacity. From the densities the compositions in weight percentage were obtained using the table in the International Critical Tables [6], which gives the composition in weight percentage corresponding to various densities at several temperatures, including 30° C. The alcohol concentrations in volume percentage at 60° F were then calculated using values of the densities of the *n*-propyl alcohol solutions at 60° F and of pure *n*-propyl alcohol at 60° F. It was necessary to obtain these density values at 60° F by interpolation from the values in the International Critical Tables at 0, 15, and 30° C. A further calculation was made to determine the volume percentage of water in each solution. Volume percentage as here used is equal to the volume in milliliters at 60° F of pure *n*-propyl alcohol and of pure water, respectively, which were mixed to make 100 ml of solution at 60° F. Since there is a contraction in volume on mixing *n*-propyl alcohol and water, the sum of the volume percentages of the two constituents exceeds 100.

After completion of measurements of separation temperatures of mixtures with gasoline, density determinations were made again on the eight stock *n*-propyl alcohol solutions to check the concentrations and to determine whether any changes due to water absorption had occurred. No changes of more than 1 part in 2,000 were observed.

In the course of the work, the preparation of additional *n*-propyl alcohol solutions was found desirable. These solutions were prepared by mixing weighed amounts of two of the eight original *n*-propyl alcohol solutions or by adding a weighed amount of water to a weighed amount of one of the *n*-propyl alcohol solutions.

III. EXPERIMENTAL PROCEDURE

The method of preparing the mixtures of gasoline with alcohol and the apparatus and procedure used in determining the separation temperatures are described in a previous paper [1].

Three gasolines were used in the present work and identification data on each are given in table 1.

TABLE 1.—*Identification data on gasolines*

Sample	Description	Distillation temperatures at stated percentages evaporated, ° C.			
		10 percent	50 percent	90 percent	Specific gravity 60°/60°
A	U. S. motor gasoline	73	121	186	0.758
B	Refinery naphtha	76	121	182	.747
C	Natural gasoline	51	58	109	.683

Critical solution temperatures of mixtures of each of these gasolines with ethyl alcohol solutions containing various percentages of water were first determined, to serve as a basis of comparison with the values obtained with *n*-propyl alcohol mixtures. The characteristic constant K for each gasoline was calculated as described in a previous paper [4]. The value of K for gasoline A is 597, for gasoline B is 628 and for gasoline C is 462. Using these values of K, critical solution temperatures of each of the three gasolines were computed. The agreement between observed and calculated values is shown graphically in figure 1. The average deviation is 1.5° C (2.7° F).

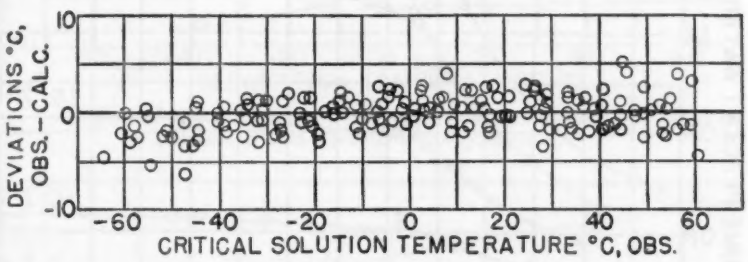

FIGURE 1.—*Comparison of calculated and observed values of critical solution temperatures of mixtures of gasolines A, B, and C with ethyl alcohol*

With each gasoline, mixtures containing 5, 10, 15, 20, and 25 percent of each of the *n*-propyl alcohol solutions were prepared. The percentage referred to as volume percentage is strictly the volume of *n*-propyl alcohol solution which, when mixed with the appropriate volume of gasoline, gives a summation of volumes equal to 100 at 60° F. Immediately after preparation the separation temperature of each mixture was determined. No measurements were made, however, unless the temperature fell between +65 and −65° C.

A large number of the separation temperatures obtained were freezing points rather than critical solution temperatures, as the second phase which appeared was solid crystals rather than liquid. It was also found that where a second liquid phase appeared, crystals were subsequently obtained on further cooling.

Duplicate determinations of the separation temperatures which were freezing points, agreed in most cases within 0.2° C. On the other hand, as may be seen in figures 2, 3, and 4, the slope of the critical-solution-temperature curves is so small that extremely minute

differences in water content make differences of many degrees in the critical solution temperature, and accordingly, in this range the reproducibility of separation temperatures is not good. This is not of any practical importance since such errors do not change the positions of these curves.

IV. EXPERIMENTAL DATA

The data obtained are shown graphically in figures 2, 3, and 4, where the volume percentage of water at 60° F in the mixture is plotted

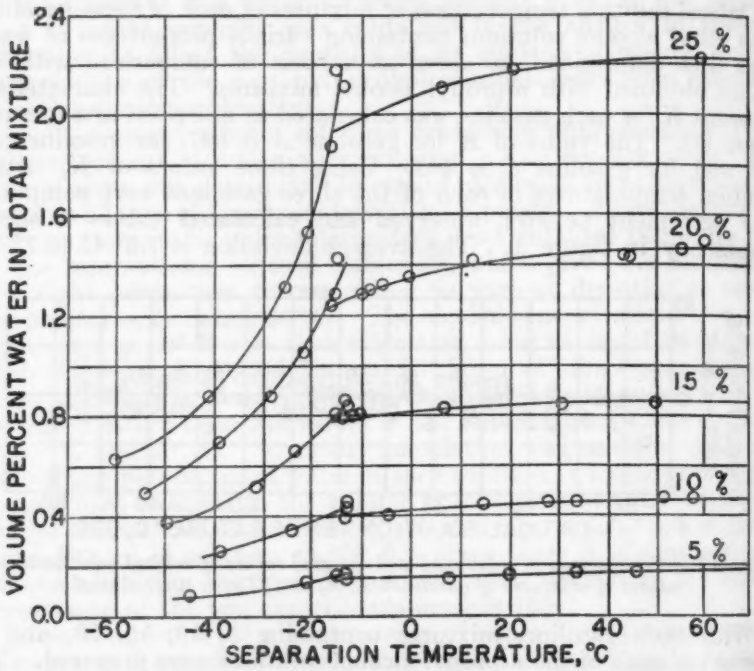

FIGURE 2.—*Effect of water content on the separation temperatures of mixtures of gasoline A with aqueous n-propyl alcohol.*

against the separation temperature. In these plots the curves on the left are freezing-point curves, while those on the right are critical-solution-temperature curves. It will be noted that freezing occurs in all cases at temperatures below about −15° C.

The water tolerances at a number of temperatures for mixtures of each of the three gasolines with *n*-propyl alcohol are given in table 2. These data are smoothed values read from plots of volume percentage of water in the mixture against separation temperature. Similar smoothed data for ethyl alcohol mixtures with these gasolines are included for comparison.

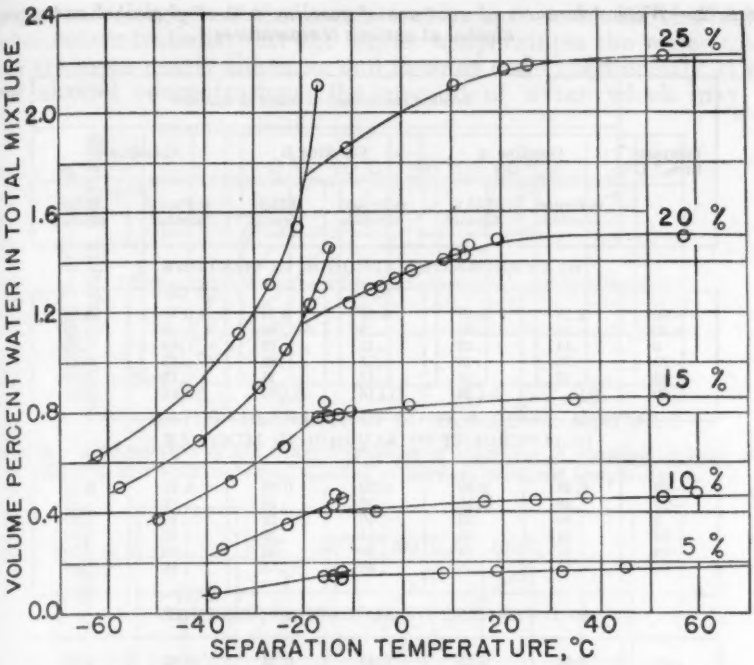

FIGURE 3.—*Effect of water content on the separation temperature of mixtures of gasoline B with aqueous n-propyl alcohol.*

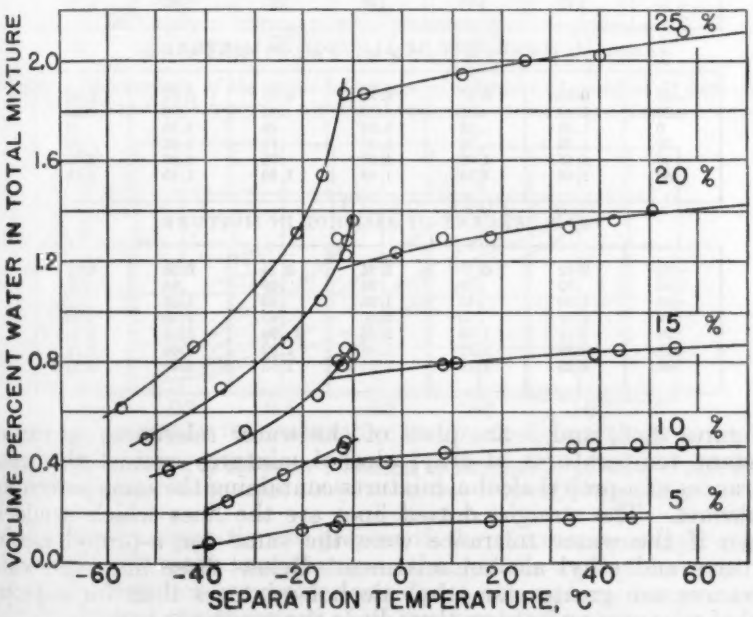

FIGURE 4.—*Effect of water content on the separation temperatures of mixtures of gasoline C with n-propyl alcohol.*

TABLE 2.—*Water tolerances of mixtures of gasoline with ethyl alcohol and n-propyl alcohol at various temperatures*

Temperature, ° C	Volume percentage of water in mixture					
	Gasoline *A*		Gasoline *B*		Gasoline *C*	
	n-Propyl alcohol	Ethyl alcohol	*n*-Propyl alcohol	Ethyl alcohol	*n*-Propyl alcohol	Ethyl alcohol
(a) 5 PERCENT OF ALCOHOL IN MIXTURE						
−40	0.08	0.04	0.07	0.04	0.07	0.06
−20	.13	.06	.12	.06	.13	.19
0	.14	.10	.13	.09	.14	.12
20	.15	.13	.15	.13	.15	.17
40	.16	.18	.17	.18	.16	.22
60	----------	.24	.18	.22	.18	.27
(b) 10 PERCENT OF ALCOHOL IN MIXTURE						
−40	0.24	0.09	0.22	0.08	0.21	0.15
−20	.38	.15	.38	.14	.38	.22
0	.40	.22	.40	.21	.42	.30
20	.44	.32	.44	.30	.44	.40
40	.46	.43	.45	.42	.45	.52
60	.46	.55	.46	.55	.46	.65
(c) 15 PERCENT OF ALCOHOL IN MIXTURE						
−40	0.43	0.15	0.46	0.14	0.42	0.25
−20	.70	.25	.73	.23	.64	.36
0	.82	.37	.82	.35	.77	.52
20	.84	.53	.84	.50	.81	.69
40	.85	.72	.85	.69	.84	.88
60	.85	.95	.86	.91	.85	1.10
(d) 20 PERCENT OF ALCOHOL IN MIXTURE						
−40	0.66	0.22	0.70	0.19	0.64	0.36
−20	1.10	.35	1.16	.32	.96	.53
0	1.36	.53	1.34	.49	1.23	.74
20	1.43	.76	1.47	.71	1.31	.99
40	1.45	1.03	1.48	.98	1.37	1.27
60	1.46	1.35	1.49	1.30	1.40	1.58
(e) 25 PERCENT OF ALCOHOL IN MIXTURE						
−60	0.62	0.16	0.64	0.14	0.58	0.31
−40	.89	.29	.94	.25	.88	.49
−20	1.60	.46	1.66	.42	1.35	.72
0	2.07	.70	2.00	.65	1.90	1.00
20	2.17	1.00	2.16	.94	1.98	1.33
40	2.20	1.37	2.21	1.30	2.03	1.70
60	2.22	1.71	2.22	1.73	2.07	2.11

Figures 5, 6, and 7 are plots of the water tolerances at various constant temperatures of ethyl alcohol mixtures against the water tolerances of *n*-propyl alcohol mixtures containing the same percentage of alcohol. The straight dotted lines are the lines which would be drawn if the water tolerance were the same for *n*-propyl alcohol mixtures and ethyl alcohol mixtures. Below these lines the water tolerances are greater for ethyl alcohol mixtures than for *n*-propyl alcohol mixtures and above these lines the reverse is true.

It is seen that in general *n*-propyl alcohol mixtures have a greater water tolerance than ethyl alcohol mixtures. The differences in this

direction are largest at the lower temperatures and with the higher alcohol concentrations. At the higher temperatures the water tolerances are more nearly the same and in some cases, particularly at the lower alcohol concentrations, the amount of water which may be

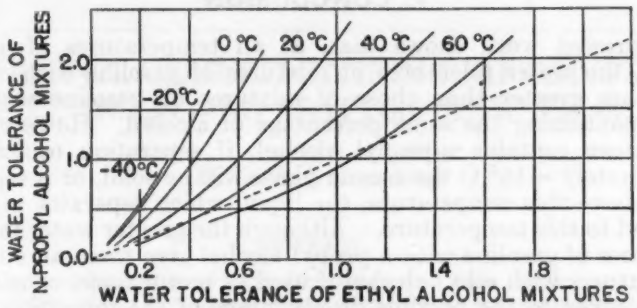

FIGURE 5.—*Comparison of the water tolerances of mixtures of gasoline A with ethyl alcohol and with n-propyl alcohol at various constant temperatures.*

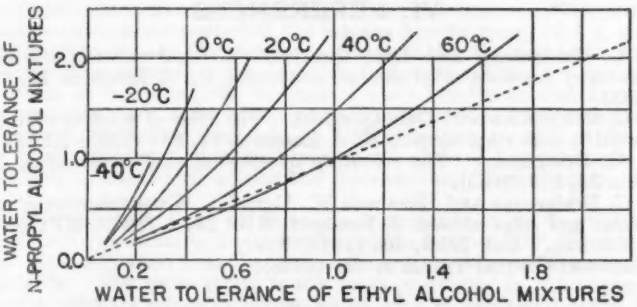

FIGURE 6.—*Comparison of the water tolerances of mixtures of gasoline B with ethyl alcohol and with n-propyl alcohol at various constant temperatures.*

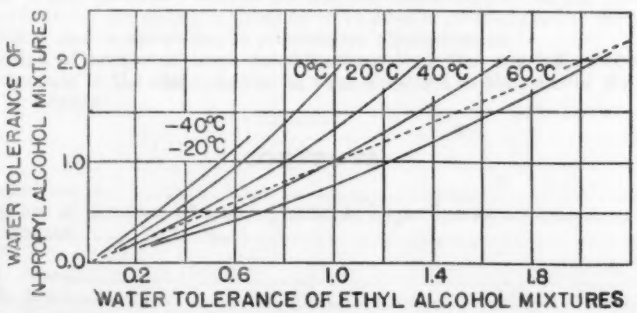

FIGURE 7.—*Comparison of the water tolerances of mixtures of gasoline C with ethyl alcohol and with n-propyl alcohol at various constant temperatures.*

present without separation is greater if the mixture contains ethyl alcohol. However, the temperatures at which the water tolerances of ethyl alcohol mixtures are greater, are above atmospheric temperature in most cases and are therefore of no practical interest.

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It should be noted that at the temperatures −40° and −20° C the material which separates is solid if the mixture contains *n*-propyl alcohol and is liquid if the mixture contains ethyl alcohol.

V. CONCLUSION

The present work shows that, at all temperatures of practical interest, the water tolerances of mixtures of gasoline with *n*-propyl alcohol are greater than those of mixtures of gasoline with ethyl alcohol containing the same percentage of alcohol. However, when the mixture contains *n*-propyl alcohol, if separation occurs below approximately −15° C the second phase will be solid, or if separation occurs above this temperature, the liquid which separates will freeze if lowered to this temperature. Although the greater water tolerances of mixtures of gasoline with *n*-propyl alcohol give them an advantage over mixtures with ethyl alcohol if used as motor fuels, consideration must be given to the possible disadvantage of the formation of solid material which does not occur in mixtures with ethyl alcohol.

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WASHINGTON, November 11, 1937.

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INTERFERENCE MEASUREMENTS IN THE FIRST SPECTRA OF NEON, ARGON, AND KRYPTON BETWEEN 4812 AND 3319 A [1]

By Curtis J. Humphreys

ABSTRACT

Wave-length measurements in the first spectra of neon, argon, and krypton have been made, using Fabry-Perot interferometers with aluminized quartz plates and etalons of 3, 7.5, 8, 8.4, 15, 20, and 25 mm length. The wave lengths have been determined relative to the adopted International Wave-Length Standards in Kr I. All but three of the 30 possible $1s-3p$ lines of Ne I are intense enough to permit interference measurements. This group lies between 3754 and 3370 A.

New measurements are reported of the intense $1s-3p$ group of A I, previously measured relative to Ne and Cd standards, but here, for the first time, relative to Kr I. The argon measurements also include 17 ultraviolet lines, the last at 3319 A.

Measurements in Kr I comprise 30 lines of wave lengths shorter than 4274 A, the limit of previous work. An additional *f*-type series has been revealed. It is now possible, by interference methods, to fix the various *p*-series of Kr I to four members. In addition, measurements were made of seven krypton lines between 4812 and 4302 A, not included among the International Wave-Length Standards of 1935.

The short wave-length limit of these measurements is set by the intensity decrement of lines approaching the series limits, the $1s$-levels (^1P, ^3P) of the noble-gas spectra. It is expected that the more-intense lines will prove useful as wave-length standards. The neon group is the most promising in this respect. The possibility of a pressure effect in higher series lines in neon and argon has been investigated to a limited extent by comparing wave lengths obtained with Geissler tubes filled with gas to "low" and "high" pressures. Without drawing general conclusions, it may be stated that no such effect was observed for the $1s-3p$ lines of neon, but that the use of argon tubes filled to 20-mm pressure led to very marked line broadening and some evidence of pressure displacement.

Construction of arrays of term combinations indicates a relative accuracy of the measurements of the same degree as that obtained in the case of the adopted secondary standards.

CONTENTS

	Page
I. Introduction	17
II. Discussion of pressure effect and isotopic hyperfine structure	18
III. Experiments	21
IV. Results	24
1. Neon	24
2. Argon	26
3. Krypton	29
V. References	32

I. INTRODUCTION

The spectra of the noble gases, particularly neon and krypton, have found considerable application as sources of wave-length stand-

[1] A preliminary report of these measurements was given at the Washington meeting of the American Physical Society, April 1937, Phys. Rev. 51, 1018A (1937).

ards for spectroscopic measurements and metrology. In 1935 the International Astronomical Union, which sponsors the specification and adoption of such standards, adopted wave-length values of 20 lines each of neon and krypton as international secondary standards [1][2]. The neon and krypton scales are regarded as agreeing with that of the primary standard, the red line of cadmium (6438.4696 A), to within 1 part in 50,000,000.

The noble-gas spectra have been the subject of numerous investigations at this Bureau, and an extensive series of interference measurements has been made. A paper by Meggers and the author [2], published in 1934, reported interference measurements in He I, Ne I, A I, Kr I, and Xe I, between 10 830 and 3948 A, and included results of previous work for comparison. It was stated there that "Geissler tubes containing noble gases are at present the most convenient and reproducible sources of secondary standards of wave length." In the same paper, the relative merits of the various noble gases, from the point of view of suitability as sources of wave-length standards, were discussed. This discussion, which included consideration of limiting orders of interference, reversibility, and isotopic hyperfine structure, need not be repeated, although some further discussion of the effect of the presence of isotopic hyperfine structures on the measurement of interference patterns will be given.

The purpose of the present investigation was twofold: First, to extend the interference measurements into the ultraviolet region, where standards are greatly needed, and also to remeasure certain visible lines, particularly in case of argon, for which additional independent observations are desirable.

Unfortunately, the number of ultraviolet noble-gas lines of sufficient intensity for interference measurements is small. Examination of the term values [3] shows why this must be true. The same discussion applies in essentials to Ne I, A I, Kr I, and Xe I. The combinations with the normal state, $s^2p^6\ {}^1S_0$ all lie in the extreme ultraviolet observable only with vacuum spectrographs.

The $1s-2p$ combinations (Paschen notation [4]) comprise the most intense visible and infrared lines of the noble-gas spectra. The $1s-3p$ lines are all ultraviolet in neon, mostly visible in argon and krypton, and all visible in xenon. (Series converging to the $2p$ levels are all visible or infrared.) The available ultraviolet lines are limited therefore to higher series members of the $1s-np$ type and a few combinations with f-type levels. The short wave-length limit to the observations is set by the intensity decrement of lines approaching the series limits, the $1s$-levels (^1P, ^3P). The first spectra of the noble gases contain no lines between the $1s_5$ limits and the extreme ultraviolet combinations. These $1s_5$ limits have been evaluated as follows: Ne, 39887.6 cm^{-1} or 2506.3 A; A, 33767.7 cm^{-1} or 2943.1 A; Kr, 32943.2 cm^{-1} or 3034.6 A; and Xe 30766.4 cm^{-1} or 3249.4 A.

II. DISCUSSION OF PRESSURE EFFECT AND ISOTOPIC HYPERFINE STRUCTURE

A possible objection to the use of ultraviolet noble-gas lines as standards is that inasmuch as they involve combinations of high

[2] Numbers in brackets refer to publications listed at the end of this paper.

levels they may be more susceptible to pressure effect than lines in the less refrangible part of the spectrum.

In 1936, Jackson [5] reported determinations relative to the cadmium primary standard of 47 visible and ultraviolet krypton lines between 6456 and 3424 A, including 14 of the ultraviolet lines measured in this investigation. He compared results from tubes filled to pressures of 0.1, 4, 10, and 20 mm of mercury. His results indicated pressure displacement proportional to the square of the pressure for any given term. The pressure shift was also found to be dependent only on the principal quantum number of the terms, within experimental error. It was concluded that the maximum operating pressures for the various krypton series, without introducing pressure shifts sufficient to affect interferometer comparisons by 0.0001 A, were as follows: for $1s-2p$, 10 mm; for $1s-3p$, 4 mm; and for $1s-4p$, less than 1 mm. The $1s-3p$ lines of neon which were observed in this investigation are analogous in origin to the blue krypton group, 4502 to 4273 A, comprising most of the adopted krypton secondary standards. One would expect the pressure effect to be of about the same magnitude for the corresponding transitions. It seems certain that no difficulty with pressure effect will be experienced if an operating pressure of the order of 1 mm is specified. The matter will be referred to again in connection with the account of our experimental work.

The effect of isotopic hyperfine structure on the wave-length measurements in neon has been the subject of considerable discussion, and it is felt that it can be treated in some detail here. The two abundant isotopes of neon are of atomic weight 20 and 22, in proportions of about 9 to 1. In the observed spectrum each neon line should have a close satellite due to isotope 22. Unless, however, the source is cooled by use of liquid air, this pattern is usually not resolved and the measured wave length will be that of the blend. The most probable comparator setting would be on the centroid of the pattern. Ritschl and Schober [6] have recently measured the isotope separation for all the strong neon lines, permitting a calculation of the displacements of a large number of terms.

Most of the $1s-2p$ lines have a separation of about 55×10^{-3} cm^{-1}, whereas in the case of the $1s-3p$ lines, it is generally about 85×10^{-3} cm^{-1}; the difference being due to the smaller displacement of higher p terms. It is apparent, therefore, that measurements of $1s-3p$ lines will be affected by isotope displacements to a slightly greater degree than those of $1s-2p$ lines. When interference patterns are measured, the effect of an unresolved satellite upon the apparent wave length depends upon the order of interference. The experience of various observers was discussed at the 1935 meeting of the IAU [7], and, in adopting the recommended standards in neon, it was agreed to specify "that they apply only to the conditions under which they were determined, viz., with interferometers of high resolving power but etalons not exceeding about 4 cm."

The following discussion based on the geometry of an interference pattern from a Fabry-Perot interferometer is intended to account for the observed results, in particular why a separation of 4 cm is some-

what critical for the neon case. The order of interference is given by

$$P=\frac{2e}{\lambda}\cos\theta, \quad [8]$$

where e is the separation (length of etalon) and θ is the angular separation of the fringe corresponding to P from the optical axis. The dispersion is given by the partial derivative

$$\frac{\delta\theta}{\delta\lambda}=-\frac{1}{\sin\theta}\frac{P}{2e}$$

Inasmuch as the ratio $P/2e$ is constant, it follows that for a given θ the separation of a satellite from a principal component will be constant. The angular separation of orders will, however, differ with retardation, and while a satellite will maintain its separation from the principal component of the same order, it will change its position with respect to the principal component of next higher or lower order. Figure 1 illustrates the interference pattern of a neon

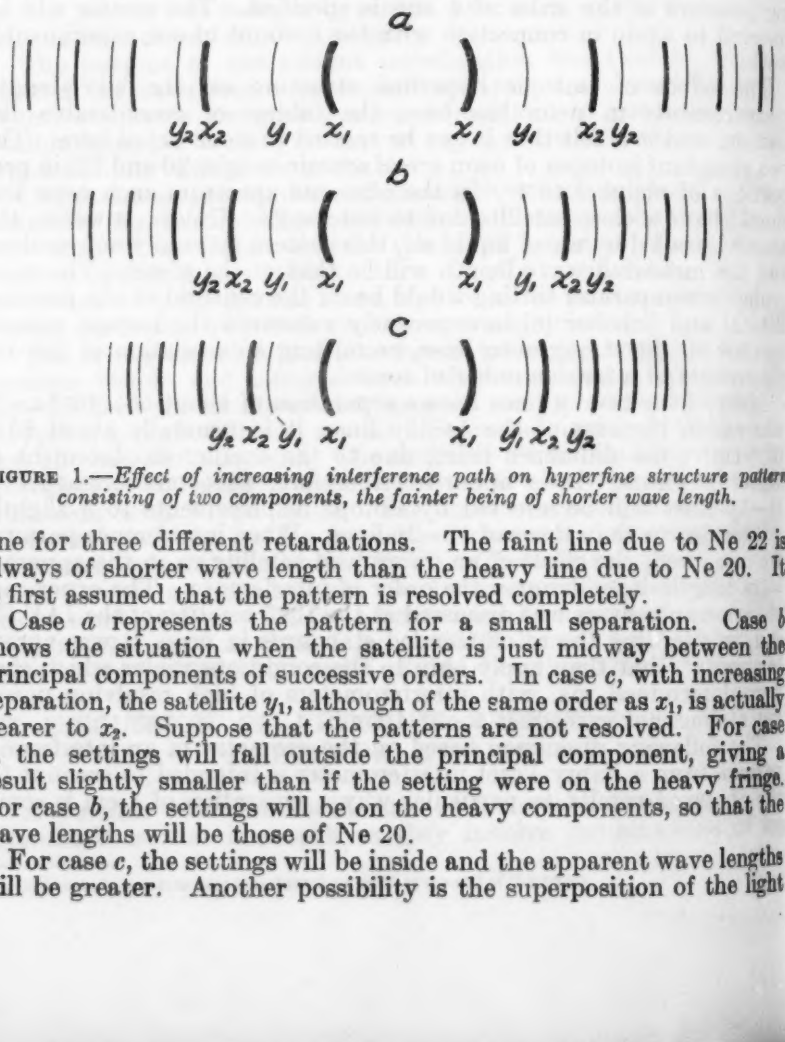

FIGURE 1.—*Effect of increasing interference path on hyperfine structure pattern consisting of two components, the fainter being of shorter wave length.*

line for three different retardations. The faint line due to Ne 22 is always of shorter wave length than the heavy line due to Ne 20. It is first assumed that the pattern is resolved completely.

Case *a* represents the pattern for a small separation. Case *b* shows the situation when the satellite is just midway between the principal components of successive orders. In case *c*, with increasing separation, the satellite y_1, although of the same order as x_1, is actually nearer to x_2. Suppose that the patterns are not resolved. For case *a*, the settings will fall outside the principal component, giving a result slightly smaller than if the setting were on the heavy fringe. For case *b*, the settings will be on the heavy components, so that the wave lengths will be those of Ne 20.

For case *c*, the settings will be inside and the apparent wave lengths will be greater. Another possibility is the superposition of the light

and heavy fringes which will occur for twice the separation corresponding to case *b*. This will give the same result as for *b*.

We see then, that there will be a cycle of increasing and diminishing apparent wave lengths. We are hardly interested in more than one phase of it, however, for that will represent the maximum path over which neon interferences can occur. Case *b* will occur for the majority of the $1s-2p$ lines with an etalon of a little less than 5 cm. If we choose one of the $1s-3p$ lines, the critical value will be slightly less than 3 cm. This discussion agrees with the experience of observers that the neon red lines have apparent wave lengths somewhat smaller, if determined with etalons of less than 4 cm length, than if greater retardations are employed. Inasmuch as we have employed etalons of 2.5 cm or less in the present investigation, the results should be on the same scale as the adopted secondary standards in neon.

III. EXPERIMENTS

The interferometer consisted of the same pair of crystal quartz plates, coated with evaporated aluminum, which were used in the recent determination of wave lengths of iron in the ultraviolet region. The coated surfaces of these plates were separated by etalons each made of three invar rods of 3, 7.5, 8, 8.4, 15, 20, or 25 mm length. All of these etalons were used only in the observations of neon.

A Littrow-type quartz spectrograph (Hilger *E1*) was employed for most of the exposures, although a few exposures were made in a Cornu prism spectrograph (Hilger *E2*). Two Zeiss quartz-fluorite objectives were available for projecting the interference pattern upon the slit of the spectrograph, one of 25 cm, the other of 50-cm focal length, the choice being determined by the length of etalon. The 25-cm projector was used in a few instances with the 7.5-mm etalon and in all cases with the 3-mm etalon. The interferometer was illuminated with parallel light by means of a quartz lens. Care was taken to line up the interferometer and all optical accessories coincident with the axis of the spectrograph. The interferometer was also placed at such a distance from the ring projector as to be focused upon the prism of the spectrograph.

All wave-length determinations here reported are relative to the krypton secondary standards in the wave-length interval between 4502 and 4274 A [1]. Krypton was chosen because of the superior sharpness of the standard lines and because the location of these lines at the lower wave-length end of the visible region simplifies comparisons with lines in the same region and in the nearby ultraviolet, and minimizes errors due to the necessity of focusing a spectrograph for widely separated regions. In making measurements in the krypton spectrum relative to krypton standards only one source is needed, affording the obvious advantage of identical conditions of illumination for all lines. The same advantage might be claimed for comparing neon ultraviolet lines with neon standards, but the intensity disparity is so great that it is practically impossible to record the first without overexposing the latter. Krypton standards seemed the obvious choice for the argon comparisons, because the blue and violet argon lines lie in the same region as the krypton standards, so that atmospheric and phase corrections are negligible over a considerable wave-length interval. It was also felt that inasmuch as previous determina-

tions had been made relative to cadmium or neon, it was advantageous to make independent comparisons with krypton.

The krypton sources were Geissler tubes purchased from Robert Götze, in Leipzig. These tubes are listed in the maker's catalog as type *D*. They have a small capillary bore, about 1.5 mm, cylindrical aluminum electrodes, and are designed for either end-on or side-on illumination. The pressures are not specified for the krypton-filled tubes, but in these experiments the discharge characteristics indicated 1 mm or less. The krypton tubes were always used in the side-on position.

Several different neon tubes were used, and part of these were of the same manufacture and type as the krypton tubes. Others were of similar design but of larger capillary bore, made by the Linde Air Products Co. Still another, filled with gas at a pressure of several millimeters, was used in a series of observations to see whether pressure displacements could be measured. No systematic variations were found in the results to indicate that wave lengths obtained from different tubes were not identical within the limits of accidental error.

Both Linde and Götze argon tubes were used. The exhaustion of our supply of "low" pressure Götze tubes early in the investigation proved something of a handicap, because the illumination from the Linde tubes was of low intensity. Götze tubes filled to a pressure of 20 mm of Hg did not prove satisfactory, because there was very noticeable line broadening and some evidence of pressure displacement. It is not felt that the present investigation warrants any conclusions regarding pressure effect, except that it is a negligible factor if the pressures within the sources are of the order of 1 mm of Hg.

The pressure in a tube filled with a noble gas diminishes during operation due to the occlusion of gas by material sputtered from the electrodes. This is the usual cause of eventual tube failure. This lowering of pressure during use makes an accurate quantitative estimate of pressure in a sealed tube practically impossible. We have already referred to the work of Jackson [5] on the pressure effect of krypton. Further quantitative measurements are desirable in view of theoretical studies which are being made [9]. In any such investigation the sources should be connected to pressure gages, permitting simultaneous accurate determinations of both wave lengths and pressures.

Because of the difference in intensities of the various lines, a very large range in exposure times was necessary to record satisfactory patterns. These ranged from a few minutes for the strongest neon lines to 16 hours for the weakest krypton lines. Patterns of krypton and neon photographed with a 3-mm etalon are reproduced in figure 2. With this interference path, the fringes of close neon pairs at 3593, 3418, and 3370 A are fully separated.

In the work with neon or argon where two sources are required, simultaneous exposures were made in most instances. This procedure necessitates such a disposition of both sources that each illuminates the apparatus in a manner optically equivalent. The usual scheme

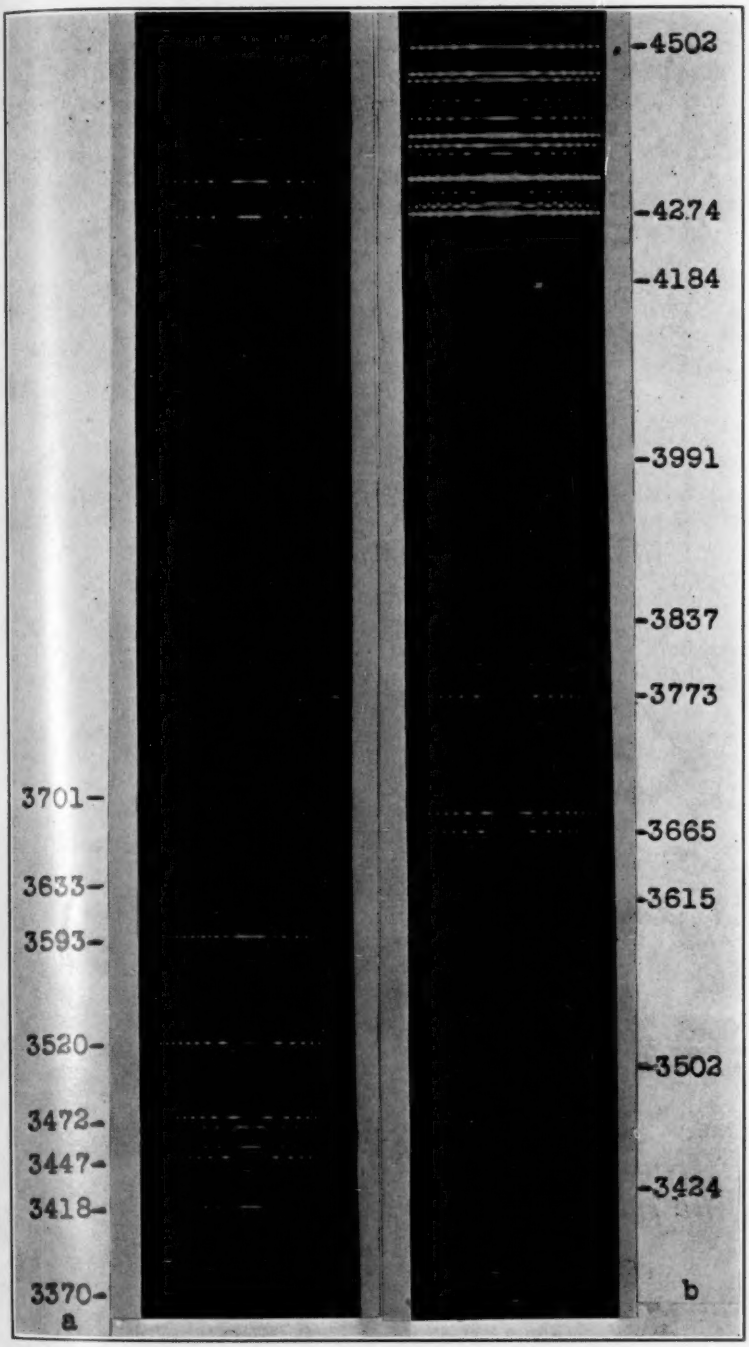

FIGURE 2.—*Fabry-Perot interference patterns of (a) neon photographed simultaneously with krypton and (b) krypton (3-mm etalon).*

is to place an inclined transparent plane mirror (a quartz plate in these experiments) between the first source and condensing lens, and reflect light from the second source into the path of the direct beam by aid of this mirror. The choice of sources for the two positions will depend on the relative intensities of the lines to be compared. A second scheme, feasible only if one of the tubes is of large capillary bore, is to place this tube in the correct position for best illumination of the interferometer. Behind the source and in line with the other units in the setup is placed a concave mirror at a distance about equal to its radius of curvature and slightly inclined to the axis. The second source is placed at the conjugate focus of this mirror and its image is brought into coincidence with the first source. In the smaller number of instances where exposures were alternated, the alternations were made frequently and the total exposure time was short, so that on the average the atmospheric conditions during the exposure of each tube could be regarded as equivalent.

The procedure of measuring, reducing, correcting, and adjusting the observations to arrive at the final reported wave-length values was carried out in accordance with methods which have been described fully in other publications. The theory of the Fabry-Perot interferometer given originally by Fabry and Buisson [10] was discussed in some detail in an earlier paper by the author [8]. The interference patterns were measured with the micrometer designed for this purpose, which is illustrated in the recent publication on interference measurements in the iron spectrum [11]. This paper also gives the details of the method of reducing observations which is followed at present. As far as possible, the same over-all size of interference pattern was measured for both primary and secondary standards. This could be accomplished conveniently by measuring the diameters of five rings in the ultraviolet and four in the region of the krypton standards. The correct order numbers for the standard lines and the length of the interference path were obtained by the method illustrated for neon by Meggers [12].

The corrections for deviations of atmospheric density from standard conditions (dry air at 15° C and 760 mm of Hg) derived from observations of the mean air temperature and barometric pressure for each exposure, were taken from tables prepared for this purpose by Meggers and Peters [13].

The corrections for dispersion of phase change at reflection were obtained by comparison of the data from 25- and 3-mm etalons, 20- and 3-mm etalons, and 7.5- and 3-mm etalons [12]. These corrections were positive below 3950 A and increased in magnitude to a maximum near 3400, amounting to about 0.001 A for the 7.5 etalon in this region. This behavior of the plates, a little surprising in view of the negative correction in the region between 3500 and 2000 A found when iron wave lengths were determined relative to neon, indicates that the correction curve has a minimum near 4000 A and a maximum near 3400 A.

IV. RESULTS

The final results of the determinations of wave length in the first spectra of neon, argon, and krypton are presented in tables 1, 3, and 5. The values were arrived at by taking a weighted mean of the averages of the corrected values obtained with the various etalons. The weights were based on the number of observations and the length of interference path, except in cases of pairs of lines most clearly resolved by certain etalons, in which cases the weights were chosen arbitrarily. The total number of observations is reported with each wave length.

Construction of arrays of term combinations, as displayed in tables 2, 4, and 6, shows that term differences are repeated to within one- or two-thousandths of a wave number in the great majority of cases. The retention of eight figures in the reported wave-length values is amply justified in all but a few cases. Calculation of the probable error of the weighted mean gave an average probable error of about 1 in the eighth place and gave a little under 3 for the neon wave length regarded as being least reliably determined. These probable errors are not reported because it is questioned if the variation in observed values, after all corrections are applied, conforms closely enough to the theory of accidental errors. For instance, it frequently happens that individual values obtained with the same etalon agree more closely than the averages from different etalons for the same line, indicating a dependence of apparent wave length upon order. Hyperfine structure or the presence of a nearby line, which may or may not be observed, can account for this, but the theory of errors is hardly applicable to such cases.

1. NEON

The adopted secondary standards of neon include most of the $1s-2p$ quantum transitions. This investigation is concerned with the next set of series members $1s-3p$. The visible blue and violet krypton, and the blue and violet argon lines originate in analogous transitions from corresponding levels in the respective atoms. The theory predicts 30 such transitions. One of these, $1s_3-3p_7$, has never been observed. Of the 29 remaining, 27 have been observed by interference methods in the present investigation. All of these are shown in table 1. A maximum of 40 exposures were recorded for some of the neon lines. This number, somewhat greater than required to arrive at satisfactory final values, was accumulated because the correction curve for dispersion of phase change at reflection showed a somewhat unexpected form in the region under investigation and an unusually large number of observations were needed to fix it precisely. Additional observations with critical lengths of interference path were also occasioned by the attempt to separate close pairs of lines. The 8.4-mm etalon was made available through the kindness of the staff of the Allegheny Observatory. Its length is very nearly one of the calculated separations required to give the optimum resolution of the close pairs of lines involving the $3p_2$ and $3p_4$ levels, which are only 0.88 cm^{-1} apart.

TABLE 1.—*Neon I interference measurements*

λ_{air}A	Number of observations	ν_{vac}cm^{-1}	Combination
3754.2160	22	26629.180	$1s_2-3p_{10}$
3701.2250	36	27010.424	$1s_2-3p_8$
3685.7359	36	27123.931	$1s_2-3p_7$
3682.2428	32	27149.660	$1s_2-3p_6$
3633.6646	38	27512.613	$1s_2-3p_5$
3609.1793	19	27699.259	$1s_3-3p_{10}$
3600.1693	38	27768.579	$1s_3-3p_9$
3593.6398	32	27819.031	$1s_3-3p_8$
3593.5259	32	27819.913	$1s_3-3p_8$
3520.4717	40	28397.194	$1s_3-3p_1$
3515.1908	38	28439.854	$1s_4-3p_8$
3510.7214	33	28476.059	$1s_3-3p^{10}$
3501.2165	39	28553.362	$1s_4-3p_7$
3498.0644	39	28579.091	$1s_4-3p_6$
3472.5711	40	28788.893	$1s_3-3p_9$
3466.5786	40	28838.658	$1s_3-3p_5$
3464.3389	38	28857.302	$1s_3-3p_9$
3460.5245	38	28889.108	$1s_3-3p_2$
3454.1952	40	28942.041	$1s_4-3p_3$
3450.7653	37	28970.808	$1s_4-3p_7$
3447.7029	40	28996.541	$1s_5-3p_6$
3423.9127	24	29198.009	$1s_4-3p_5$
3418.0066	25	29248.461	$1s_4-3p_2$
3417.9036	40	29249.342	$1s_4-3p_4$
3375.6498	6	29615.450	$1s_5-3p_5$
3369.9081	38	29665.909	$1s_5-3p_2$
3369.8086	24	29666.784	$1s_4-3p_4$

The complete array of term combinations, $1s-2p$ and $1s-3p$, have been assembled in table 2. Except for 29615.450 cm^{-1}, which is the faintest of the group, and 29666.784 cm^{-1} which is difficult to measure on account of proximity to 29665.909 cm^{-1}, the relative accuracy of the $1s-3p$ group is fully equal to that shown in the $1s-2p$ array, which includes all the adopted neon secondary standards. The remaining eight-figure wave numbers of visible and infrared lines appearing in table 2 are averages of the determinations relative to cadmium and neon reported by Meggers and Humphreys in 1934 [2]. A few seven-figure values required to complete the table are quoted from Paschen [4]. Only interferometer determinations are considered in estimating term values or relative accuracy. The term values shown in table 2 are revised to give the best agreement with all the experimental material. The difference, calculated minus observed wave number, is recorded beneath the last figure of each wave number value, considered in adopting term values. The average deviation of calculated term combinations from the observed wave numbers is 1 part in 20,000,000. Calculated values of wave numbers of lines too faint to be observed by interferometers are shown in parenthesis beneath values resulting from measurements of grating spectrograms.

TABLE 2.—*Neon 1 array of 1s—2p and 1s—3D combinations*

Term symbol ↓	J ↓	Term value ↓	$1s_2$ $J=1$ 38040.730	Diff. 1070.079	$1s_3$ 0 39110.809	Diff. 359.353	$1s_4$ 1 39470.163	Diff. 417.448	$1s_5$ 2 39887.610
$3p_1$	0	9643.536	28397.194		•		29826.65 (6.626)		•
$3p_2$	1	10221.701	27819.031 −2	1070.077	28889.108 ±0	359.353	29248.461 ±0	417.448	29665.909 ±0
$3p_3$	0	10528.119	27512.613 −2		•		28942.041 +2		•
$3p_4$	2	10220.819	27819.913 −2		•	----	29249.342 +1	417.442	29666.784 +7
$3p_5$	1	10272.152	27768.579 −1	1070.079	28838.658 −1	359.351	29198.009 +1	417.441	29615.450 +8
$3p_6$	2	10891.070	27149.660 ±0		•		28579.091 +1	417.450	28996.541 −1
$3p_7$	1	10916.800	27123.931 −1				28553.362 ±0	417.446	28970.808 +2
$3p_8$	2	11030.307	27010.424 −1		•		28439.854 +1	417.448	28857.302 +1
$3p_9$	3	11098.717	•		•	•	•		28788.893
$3p_{10}$	1	11411.550	26629.180 ±0	1070.079	27699.259 ±0		28058.69 (8.612)		28476.059 +1
$2p_1$	0	20958.703	17082.027 ±0		•		18511.459 ±0		•
$2p_2$	1	22890.987	15149.743 ±0	1070.078	16219.821 +1	359.354	16579.175 ±0	417.448	16996.623 ±0
$2p_3$	0	23012.009	15028.71		•		16458.153		•
$2p_4$	2	23070.932	14969.798 ±0		•		16399.231 −1	417.447	16816.678 ±0
$2p_5$	1	23157.328	14883.402 ±0	1070.079	15953.481 ±0	359.350	16312.831 +3	417.451	16730.282 ±0
$2p_6$	2	23613.579	14427.150 +1		•		15856.582 +1	417.450	16274.032 −1
$2p_7$	1	23807.849	14232.880 +1	1070.079	15302.959 +1	359.355	15662.314 −1	417.447	16079.761 ±0
$2p_8$	2	24105.219	13935.509 +2		•		15364.943 ±0	417.448	15782.391 ±0
$2p_9$	3	24272.400	•		•		•		15615.210
$2p_{10}$	1	25671.654	12369.076 ±0	1070.079	13439.155 ±0	359.353	13798.508 ±0	417.450	14215.958 −2

2. ARGON

The suitability of argon lines as standards, on account of extreme homogeneity and freedom from structure, was recognized at the 1935 meeting of the IAU. The repetition and extension of measurements were recommended. The results given in table 3 include determinations relative to krypton of 40 lines over the range from 4702 to 3319 A. Etalons of 15, 20, and 25 mm length were used in the comparisons. The sources used did not give very intense spectra, so that a number of ultraviolet lines remain, which could be observed by interference methods if sufficiently bright sources were employed. The earlier measurements of Meggers and Humphreys [2] and of Meggers [16] are included in table 3 for comparison insofar as they are within the wave-length range covered by this investigation. The agreement with Meggers' seven-figure values, published in 1921, is somewhat closer than with the 1934 results of Meggers and Humphreys. The latter are systematically lower, the difference being a little over 0.001 A for most lines. While we are certain that the relative accuracy of the 1934 values is at least as good as that of the results here reported, it still seems most probable that the systematic error is in the measurements of 1934.

TABLE 3.—*Argon I interference measurements*

λ_{air}, Kr standard	Number of observations	Meggers and Humphreys [2] Cd standard	Meggers and Humphreys [2] Ne standard	Meggers [16] Cd standard	ν_{vac} cm^{-1} Kr standard	Combination
A		A	A	A		
4702.3164	11		3151	317	21260.184	$1s_3-3p_{10}$
4628.4410	10		4398	445	21599.518	$1s_2-3p_8$
4596.0970	11		0964	096	21751.516	$1s_3-3p_7$
4522.3238	11		3216	325	22106.347	$1s_3-3p_{16}$
4510.7333	13	7324	7322	733	22163.149	$1s_2-3p_5$
4345.1682	13		1666	168	23007.623	$1s_3-3p_4$
4335.3380	13	3363	3370		23059.791	$1s_2-3p_3$
4333.5612	13	5601	5595	561	23069.245	$1s_3-3p_3$
4300.1011	13	1000	0995	101	23248.750	$1s_4-3p_8$
4272.1690	13	1678	1680	169	23400.751	$1s_4-3p_7$
4266.2867	13	2855	2853	286	23433.014	$1s_4-3p_6$
4259.3618	13	3607	3603	362	23471.111	$1s_2-3p_1$
4251.1852	13		1842	184	23516.254	$1s_5-3p_{10}$
4200.6751	13	6738	674	676	23799.015	$1s_5-3p_9$
4198.3170	13	3160	316	316	23812.383	$1s_4-3p_5$
4191.0296	7	0270		027	23853.787	$1s_3-3p_4$
4190.7127	7	7098		714	23855.591	$1s_5-3p_8$
4181.8838	13	8825	8826	884	23905.955	$1s_3-3p_3$
4164.1800	13	1789	1788	180	24007.587	$1s_5-3p_7$
4158.5906	13	5895	5896	591	24039.854	$1s_3-3p_5$
4054.5254	7		5250		24656.860	$1s_4-3p_4$
4045.9658	7				24709.022	$1s_4-3p_3$
4044.4182	13		4173	419	24718.477	$1s_4-3p_3$
3948.9788	13		977	980	25315.863	$1s_3-3p_2$
3947.5043	9				25325.319	$1s_3-3p_3$
3894.6602	6				25668.934	$1s_3-4p_{10}$
3834.6785	12				26070.436	$1s_3-4p_5$
3781.3609	2				26438.023	$1s_4-4X$
3770.3688	2				26515.098	$1s_3-4p_{10}$
3690.8957	7				27086.013	$1s_3-4Y$
3649.8324	9				27390.742	$1s_2-4p_1$
3634.4605	8				27506.588	$1s_4-4p_7$
3632.6837	8				27520.042	$1s_4-4p_6$
3606.5224	12				27719.664	$1s_4-4p_5$
3567.6565	13				28021.631	$1s_3-4p_9$
3554.3061	13				28126.882	$1s_3-4p_6$
3461.0780	5				28884.489	$1s_4-4p_3$
3393.7517	5				29457.490	$1s_5-5p_4$
3373.481	2				29634.49	$1s_4-5p_3$
3319.3446	3				30117.793	$1s_3-5p_6$

The argon lines lie in the same wave-length region as the blue and violet krypton standards, eliminating the possibility of an error in the new measurements due to the spectrograph not being focused exactly alike for both sources, or an error due to incorrect estimate of the correction for dispersion of phase change at reflection. An error of the kind first mentioned is possible when a prism spectrograph is being used and comparisons are being made, relative to standards in the red region, of lines in the blue or ultraviolet. The reason is that the patterns due to the standard lines appear at one end of the plate where the focusing is less satisfactory than at the center. The plate curvature in such a spectrograph gives only a fair approximation to the true focal surface. The difficulty is somewhat increased by the fact that the spectrograph is slightly astigmatic, and it is necessary to choose the most satisfactory compromise between the best adjustments for vertical and horizontal images, this compromise to be the same, if possible, for all spectral regions.

TABLE 4.—*Argon I array of 1s—np combinations*

Term symbol ↓	J ↓	Term value ↓	$1s_2$ $j=1$ 31711.630	Diff. 846.163	$1s_3$ 0 32557.793	Diff. 803.068	$1s_4$ 1 33360.861	Diff. 606.839	$1s_5$ 2 33967.700
$4p_1$	0	4320.888	27390.742		•		29039.69 (9.973)		•
$4p_2$	2	4476.372	27235.47 (5.258)		•		28884.489		29491.39 (1.328)
$4p_3$	0	5641.196	26070.436 −..		•		27719.664 +1		•
$4p_4$	2	5840.818	25870.87 (0.812)		•		27520.042 +1	606.840	28126.882 ±0
$4p_7$	1	5854.273	25857.35 (7.357)		26703.55 (3.520)		27506.588		28113.72 (3.427)
$4p_9$	3	5946.069	•		•		•		28021.631
$4p_{10}$	1	6042.696	25668.934 ±0	846.164	26515.098 −1		27318.38 (8.165)		
$3p_1$	0	8240.519	23471.111		•		25120.41 (0.342)		•
$3p_2$	1	8651.838	23059.791 +1	846.164	23905.955 ±0	803.067	24709.022 +1	606.841	25315.863 −1
$3p_3$	2	8642.383	23069.245 +2		•		24718.477 +1	606.842	25325.319 −2
$3p_4$	1	8704.006	23007.623 +1	846.164	23853.787 ±0	803.073	24656.860 −5		
$3p_5$	0	9548.480	22163.149 +1		•		23812.383 −2		•
$3p_6$	2	9927.846	21783.78 (3.784)		•		23433.014 +1	606.840	24039.854 ±0
$3p_7$	1	9960.113	21751.516 +1		22597.75 (7.680)		23400.751 −3	606.836	24007.587 ±0
$3p_8$	2	10112.111	21599.518 +1		•		23248.750 ±0	606.841	23855.591 −2
$3p_9$	3	10168.685	•		•		•		23799.015
$3p_{10}$	1	10451.446	21260.184 ±0	846.163	22106.347 ±0		22909.44 (9.415)		23516.254 ±0
$2p_1$	0	18388.832	13322.799 −1		•		14972.027 +2		•
$2p_2$	1	19615.037	12096.593 ±0	846.163	12942.756 ±0	803.068	13745.824 ±0	606.839	14352.663 ±0
$2p_3$	2	19821.753	11889.877 ±0		•		13539.108 ±0	606.839	14145.947 ±0
$2p_4$	1	19979.745	11731.885 ±0	846.163	12578.048		13381.08 (1.116)		13987.955 ±0
$2p_5$	0	20057.181			•		13303.680		•
$2p_6$	2	20873.903	10837.727 ±0		•		12486.959 −1	606.838	13093.797 ±0
$2p_7$	1	21024.195	10687.435 ±0	846.163	11533.598 ±0	803.068	12336.666 ±0	606.839	12943.505 ±0
$2p_8$	2	21494.185	10217.445 ±0		•		11866.676 ±0	606.838	12473.514 +1
$2p_9$	3	21648.696	•		•		•		12319.004
$2p_{10}$	1	23009.356	8702.31 (2.274)		9548.437 ±0	803.068	10351.505 ±0	606.838	10958.343 +1

The array of argon term combinations shown in table 4 follows the same plan as the corresponding array for neon with the addition of a few $1s-4p$ transitions for which wave numbers determined by interference measurements are available. All eight figures wave numbers in the $1s-3p$ and $1s-4p$ arrays are from the results of this investigation. The $1s-2p$ array is assembled from the interference measurements by Meggers and Humphreys [2]. The values used are the averages of the determinations relative to cadmium and those relative to neon. The few seven-place wave numbers required to complete the array are Meissner's [14]. The term values are adjusted from the interference determinations. The relative accuracy of the measurements, which can be judged from the agreement of the observed with calculated wave numbers, and the constancy of repeated term differences is of the same order as that shown by the neon array.

3. KRYPTON

The possibility of making interference measurements of ultraviolet krypton lines became apparent when a number of them appeared among the $1s-3p$ neon lines which were being determined relative to krypton. By rather long exposures, it was possible to obtain measurable patterns for 30 ultraviolet lines. Measurements were made on several fourth members of $1s-np$-type series, permitting the evaluation of all but one of the $5p$ terms by interference measurements. Several combinations of f type terms were observed. Two lines, 3837.8162 and 3503.8981 A, were shown by more precise measurements to be first and second members of a new series, $1s_5-n$T, and not $1s_5-n$Y, as at present classified [15]. The T series of terms have j-value, 3, and combine only with s_5. A new line, 3837.7028 A, was revealed as a close companion to 3837.8162 A and is properly classified as $1s_5-4$Y. Interference measurements were made of seven lines not included in the list of secondary standards but lying in the same region. Etalons of 3, 7.5, 20, and 25 mm length were used in the wave-length comparisons, the results of which are assembled in table 5, together with the results of previous measurements in the same wave-length interval.

TABLE 5.—*Krypton 1 interference measurements*

λ_{air} Kr standard	Number of observations	Jackson [5] Cd standard	Humphreys [8] Ne standard	Meggers and Humphreys [2] Ne standard	ν_{vac} cm^{-1} Kr standard	Combination
A		A	A	A		
4812.6367	4		607		20772.843	$1s_3-4$X
4550.2985	5	2985	298		21970.441	$1s_4-3p_{10}$
4425.1908	8	1906	1909	190	22591.573	$1s_2-3p_4$
4418.7626	8	764	769		22624.437	$1s_3-5$Z
4416.8838	5				22634.061	$1s_3-5$X
4410.3685	8	3687	369		22627.498	$1s_3-3p_3$
4302.4455	3				23236.081	$1s_3-5p_{10}$
4263.2881	4				23449.496	$1s_3-5p_8$
4184.4726	7				23891.164	$1s_3-5p_{10}$
3991.2581	10				25047.699	$1s_4-4$X
3991.0797	11				25048.818	$1s_4-4$Z
3982.1699	5				25104.862	$1s_4-4$Y
3845.9778	9				25993.845	$1s_3-4$Z
3837.8162	10	8162			26049.122	$1s_5-4$T
3837.7028	2				26049.892	$1s_5-4$Y
3812.2155	11	2159			26224.049	$1s_4-4p_3$
3800.5437	11	5440			26304.584	$1s_4-4p_7$
3796.8839	11	8844			26329.938	$1s_4-4p_8$
3773.4241	15	4247			26493.630	$1s_4-4p_8$
3698.0452	17	047			27033.649	$1s_3-4p_{10}$
3679.6111	9				27169.078	$1s_3-4p_3$
3679.5609	22				27169.448	$1s_3-4p_5$
3668.7363	10	7374			27249.609	$1s_3-4p_7$
3665.3259	22	3263			27274.963	$1s_3-4p_8$
3632.4896	5				27521.512	$1s_4-3p_4$
3628.1570	9	1571			27554.376	$1s_4-5$Z
3615.4755	11	4749			27651.022	$1s_4-3p_2$
3540.9538	6				28232.940	$1s_4-5p_7$
3539.5416	6				28244.204	$1s_4-5p_8$
3522.6747	10	675			28379.436	$1s_4-5p_3$
3511.8963	6				28466.533	$1s_2-3p_4$
3503.8981	7				28531.510	$1s_5-5$T
3502.5537	11				28542.461	$1s_5-3p_2$
3495.9900	7	9897			28596.049	$1s_3-3p_2$
3434.1423	5				29111.037	$1s_3-5p_{10}$
3431.7217	10	7511			29131.571	$1s_3-5p_3$
3424.9433	10	9720			29189.224	$1s_3-5p_4$

Jackson's [5] observations in the ultraviolet were made using a krypton tube filled to 4-mm pressure, whereas ours were with pressures of 1 mm or less. The small but systematic difference between the two sets of values for the $1s-4p$ transitions is in essential agreement with Jackson's estimated pressure shifts. No attempt is made to explain the disagreement of Jackson's wave lengths of the lines 3431.7217 and 3424.9433 A with ours. Only the second value can be checked from the term array, but our value of the wave number 29189.224 cm^{-1} gives a fair fit, whereas Jackson's is outside the range of accidental error. Previous National Bureau of Standards' measurements of the visible lines included in the data were all from relatively faint patterns. The standards, and consequently the fainter lines, were not so heavily exposed as is necessary when making comparisons with ultraviolet lines. The agreement is, therefore, considered satisfactory. The disagreement of the 1930 [8] value for 4812 A was owing to an incorrect choice of order in the single available determination. A recheck of the original determination shows that it should have given 4812.636 A.

Construction of the array of $1s-np$ term combinations in krypton, leads to a somewhat more extensive table than is the case with neon or argon, if all wave numbers determined by interference measurements are included. This is attributable to the appearance of higher series members in the more accessible part of the ultraviolet region. Such an array is shown in table 6. The wave numbers there assembled include all results of this investigation, all krypton secondary standards [1] which are represented by transitions of $1s-np$ type, and the 1934 interference measurements by Meggers and Humphreys [2] of lines not included in the first two groups. The third group, consisting mostly of infrared, had been determined relative both to cadmium and neon. An average was adopted for use in this array. A considerable number of $1s-np$ transitions give lines too faint for interference measurements. For the sake of completeness, these are included in the table, the values being given by the latest National Bureau of Standards grating observations [15]. As in the previous cases, the term values have been adjusted to give the best conformity to the entire set of interference observations. The relative accuracy of the ultraviolet determinations compares favorably either with that of the secondary standards or the group of infrared lines.

Calculated values of wave numbers in the inaccessible infrared region are shown in parentheses.

Attention is called to a similar array published in 1930 [8] using the measurements then available, but not including ultraviolet data. It will be seen that the changes due to repeated measurements of increased precision are practically negligible.

TABLE 6.—*Krypton I array of 1s—np combinations*

Term symbol	j	Term value	$1s_2$ $j=1$ 27068.199	Diff. 655.087	$1s_3$ 0 27723.286	Diff. 4274.853	$1s_4$ 1 31998.139	Diff. 945.026	$1s_5$ 2 32943.165
5T	3	4411.655	•		•		•		28531.510
5X	1	4434.138	22634.061		23289.16		27563.85		28509.04
					(9.148)		(4.001)		(9.027)
5Z	2	4443.763	22624.437		•		27554.376		28449.45
			−1				±0		
$5p_1$	0	3618.703	23449.496		•		28379.436		•
			±0				±0		
$5p_2$	2	3753.938	23314.25		•		28244.204	945.020	29189.224
			(4.261)				−3		+3
$5p_3$	1	3765.199			23957.82		28232.940		29177.92
					(8.087)				(7.966)
$5p_4$	3	3811.594	•		•		•		29131.571
$5p_{10}$	1	3832.120	23236.081	655.083	23891.164		28165.44		29111.037
			−2		+2		(6.019)		+8
4T	3	6894.043	•		•		•		26049.122
4X	1	6950.442	20117.72		20772.843	4274.856	25047.699		25992.88
			(7.757)		+1		−2		(2.723)
4Y	2	6893.275	20174.92		•		25104.862	945.030	26049.892
			(4.924)				+2		−2
4Z	2	6949.321	20118.85		•		25048.818	945.027	25993.845
			(8.878)				±0		−1
$4p_1$	0	5504.509	21563.65		•		26493.630		•
			(3.690)						
$4p_2$	2	5668.201	21399.92		•		26329.938	945.025	27274.963
			(9.998)				±0		+1
$4p_3$	1	5693.555	21374.53		22029.69		26304.584	945.025	27249.609
			(4.644)		(9.731)		±0		+1
$4p_4$	2	5774.089	21294.04		•		26224.049	945.029	27169.078
			(4.010)				+1		−2
$4p_5$	3	5773.717	•		•		•		27169.448
$4p_{10}$	1	5909.516	21158.61						27033.649
			(8.683)						
$3p_1$	0	4093.318	22974.881		•				•
$3p_2$	2	4347.117	22721.082		•		27651.022	945.027	28596.049
			±0				±0		−1
$3p_3$	1	4400.701	22667.498	655.087	23322.585		27597.18		28542.461
			±0		±0		(7.438)		+3
$3p_4$	1	4476.626	22591.573	655.087	23246.660	4274.852	27521.512	945.021	28466.533
			±0		±0		+1		+6
$3p_5$	0	9153.254	17914.93		•		22844.885		•
			(4.945)						
$3p_6$	2	9552.275	17515.93		•		22445.864	945.026	23390.890
			(5.924)				±0		±0
$3p_7$	1	9601.416	17466.81		18121.89		22396.723	945.025	23341.748
			(6.783)		(1.870)		±0		+1
$3p_8$	2	9793.947	17274.47		•		22204.392	945.027	23149.419
			(4.252)				±0		−1
$3p_9$	3	9799.251	•		•		•		23143.914
$3p_{10}$	1	10027.698	17040.53		17695.585	4274.856	21970.441	945.029	22915.470
			(0.501)		+3		±0		−3
$2p_1$	0	14059.829	13008.370		•		17938.27		•
							(8.310)		
$2p_2$	2	14969.730	12098.469		•		17028.409	945.027	17973.436
			±0				±0		−1
$2p_3$	1	14995.749	12072.450	655.087	12727.537		17002.42		17947.417
			±0		±0		(2.390)		−1
$2p_4$	1	15318.982	11749.218	655.087	12404.305	4274.852	16679.157	945.025	17624.182
			−1		−1		±0		+1
$2p_5$	0	18822.038	(8246.161)		•		13176.101		•
$2p_6$	2	19791.560	(7276.639)		•		12206.579	945.027	13151.606
							±0		−1
$2p_7$	1	19950.506	(7117.693)		(7772.780)		12047.633	945.026	12992.659
							±0		±0
$2p_8$	2	20607.523	(6460.673)		•		11390.616	945.027	12335.643
							±0		−1
$2p_9$	3	20620.501	•		•		•		12322.664
$2p_{10}$	1	21746.387	(5321.812)		(5976.899)		10251.751	945.027	11196.778
							+1		±0

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INFRARED SPECTRA OF IRON, TITANIUM, AND CARBON

By Carl C. Kiess

ABSTRACT

New wave lengths in the arc spectra of iron and titanium have been recorded photographically with the type *Z* plates produced by the Kodak Research Laboratories. The long wave-length limits of these spectra have now been extended to the vicinity of 12 000 A. Many of the observed lines were predictable from previously known terms. Several apparently related groups of lines in titanium have revealed a new term, e'^3P, belonging to the third set and combining with terms of the middle set. Previously known lines in the spectrum of carbon have been photographed with high dispersion to obtain accurate wave-length values for use in identifying infrared lines in the sun's spectrum. A new band in the infrared system of CN has been found.

CONTENTS

	Page
I. Introduction	33
II. Results	33
1. Iron	33
2. Titanium	35
3. Carbon	37

I. INTRODUCTION

In this journal,[1] five years ago, were presented descriptions of the infrared spectra of several elements which, with the aid of the new types of plates brought out by the Research Laboratories of the Eastman Kodak Co., extended the limits of photographically recorded wave lengths to the neighborhood of 11 000 A. Since that time new sensitizers, the pentacarbocyanines,[2] have been synthesized, with which plates, sensitive out to wave length 13 000 A and beyond, have been prepared. It is the purpose of this paper to present the results that have been obtained with these new plates for iron, titanium, and carbon. The methods and apparatus employed in this investigation were the same as those described in the earlier work mentioned above.

II. RESULTS

1. IRON

The new infrared wave lengths of iron are listed in table 1. These lines were recorded on the *Z* plates with exposures, ranging from 1 to 2 hours, to a d-c arc operated on 6 or 8 amperes from a 220-volt circuit. The intensities given for the lines are the usual eye estimates, but from the low order of the assigned numbers it can be seen that

[1] W. F. Meggers and C. C. Kiess, BS J. Research, **9**, 309(1932) RP473.
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in this region iron has no lines of suitable strength for standards. The classifications of the lines given in the last column are based on known terms taken from the work of Burns and Walters,[3] or from Catalán.[4] No new terms have been found.

TABLE 1.—*Wave lengths in the infrared spectrum of iron*

λ_{air} A	Intensity	ν_{vac} cm^{-1}	Term combination
11973.01	8	8349.84	$a\,^5P_3-z\,^5D_4^\circ$
11884.12	3	8412.29	$a\,^5P_1-z\,^5D_2^\circ$
11882.80	7	8413.22	$a\,^5P_2-z\,^5D_3^\circ$
11783.28	6	8484.28	$b\,^3P_2-z\,^3D_3^\circ$
11689.98	8	8551.99	$a\,^5P_1-z\,^5D_1^\circ$
11638.25	7	8590.00	$a\,^5P_3-z\,^5D_3^\circ$
11607.57	12	8612.70	$a\,^5P_2-z\,^5D_2^\circ$
11593.55	5	8623.13	$a\,^5P_1-z\,^5D_0^\circ$
11439.06	15	8739.59	$b\,^3P_1-z\,^3D_2^\circ$
11422.30	6	8752.41	$a\,^5P_2-z\,^5D_1^\circ$
11374.02	3	8789.56	$a\,^5P_3-z\,^5D_2^\circ$
11355.97	1	8803.53	
11298.83	3	8848.05	$b\,^3P_2-z\,^3D_2^\circ$
11251.09	3	8885.60	$b\,^3P_0-z\,^3D_1^\circ$
11149.34	2	8966.69	$b\,^3P_2-z\,^3F_3^\circ$
11119.80	10	8990.51	$b\,^3P_1-z\,^3D_1^\circ$
11045.6	1*h*	9050.92	
11013.27	1	9077.47	$y\,^3D_3^\circ-e\,^5F_3$
11004.28	1	9084.89	
10991.70	1	9095.28	
10946.52	1	9132.82	
10936.00	1	9141.61	
10925.80	1	9150.14	
10896.30	3	9174.92	$4M_2-z\,^3P_2^\circ$
10886.81	1	9182.91	
10884.30	3	9185.03	
10881.65	1	9187.27	$b\,^3P_1-z\,^3F_2^\circ$
10863.60	5	9202.53	$y\,^3D_3^\circ-e\,^5F_4$
10849.68	2	9214.34	
10845.62	1	9217.79	
10825.32	1	9235.08	
10818.36	3	9241.02	
10783.09	3	9271.24	
10760.62	1	9290.61	
10752.99	3	9297.20	
10735.46	2	9312.37	
10718.38	2	9327.22	
10532.21	10	9492.09	
10469.59	20	9548.85	
10452.70	5	9564.29	
10435.17	0*b*	9580.36	$y\,^3D_3^\circ-e\,^5F_2$
10423.65	3	9590.95	$4\,M_2-z\,^3P_1^\circ$
10422.99	0	9591.55	$a\,^5G_3-z\,^3F_4^\circ$
10400.94	1	9611.88	

[3] K. Burns and F. M. Walters, jr. Pub. Allegheny Observatory 6, 159(1929).
[4] M. A. Catalán. Anales soc. españ. fís. quím. 28, 1239(1930).

2. TITANIUM

Nearly all the new lines of Ti I listed in table 2 were predictable from the previously known terms of this spectrum. These terms, owing largely to the work of Russell,[5] are listed by Miss Moore with the designations or symbols now in use.[6] To these is added a new term, $e'\ ^3P$, revealed by the present investigation. Its components, with their inner quantum numbers, are:

$e'\ ^3P_2$	34535.04
	207.08
$e'\ ^3P_1$	34327.96
	157.01
$e'\ ^3P_0$	34170.95

TABLE 2.—*Wave lengths in the infrared spectrum of titanium*

λ_{air}A	Intensity	ν_{vac}cm^{-1}	Term combination
11973. 88	6	8349. 23	$b\ ^3F_4-z\ ^3D_3^0$
11949. 58	5	8366. 20	$b\ ^3F_3-z\ ^3D_2^0$
11892. 85	5	8406. 12	$b\ ^3F_2-z\ ^3D_1^0$
11830. 36	0*b*	8450. 51	$v\ ^3D_3^0-f\ ^3F_3$ / $y\ ^3G_3^0-e\ ^3G_3$
11797. 24	3	8474. 24	$b\ ^3F_2-z\ ^3D_2^0$
11780. 54	4	8486. 25	$b\ ^3F_3-z\ ^3D_3^0$
11675. 11	2	8562. 88	
11667. 46	2	8568. 50	$c\ ^3P_2-x\ ^3D_3^0$
11652. 16	0	8579. 75	$v\ ^3D_3^0-f\ ^3F_4$
11647. 48	0	8583. 20	
11641. 91	0	8587. 30	
11635. 16	0	8592. 29	$c\ ^3P_1-x\ ^3D_2^0$
11609. 41	3	8611. 34	
11539. 50	5	8663. 51	
11403. 89	8	8766. 54	
11381. 53	7	8783. 76	
11354. 90	2	8804. 36	
11316. 72	2	8834. 06	$z\ ^3P_2^0-e'\ ^3P_1$
11292. 43	6	8853. 07	$y\ ^3D_1^0-e'\ ^3P_0$
11246. 88	8	8888. 92	$y\ ^3D_2^0-e'\ ^3P_1$
11243. 90	10	8891. 28	$y\ ^3D_3^0-e'\ ^3P_2$
11230. 91	5	8901. 56	
11144. 74	1	8970. 39	
11095. 79	5	9009. 96	$y\ ^3D_1^0-e'\ ^3P_1$
11057. 58	3	9041. 08	$z\ ^3P_1^0-e'\ ^3P_2$
10990. 70	3	9096. 11	$y\ ^3D_2^0-e'\ ^3P_2$
10977. 90	2	9106. 72	$x\ ^3F_4^0-e\ ^3G_4$
10974. 50	2	9109. 54	
10905. 08	1	9167. 53	
10899. 13	1	9172. 54	$x\ ^3F_3^0-e\ ^3G_3$
10896. 10	8	9174. 24	$x\ ^3F_4^0-e\ ^3G_5$
10855. 15	1	9209. 70	
10853. 14	3	9211. 40	
10847. 72	1	9216. 00	$a\ ^5F_3-z\ ^5G_2^0$
10833. 66	3	9227. 97	$x\ ^5D_3^0-f\ ^5F_3$

[5] H. N. Russell. Astrophys. J. 66, 347 (1927).
[6] C. E. Moore. Term Designations for Excitation Potentials, p. 12, (Princeton University Observatory, 1934).

TABLE 2.—*Wave lengths in the infrared spectrum of titanium*—Continued

λ_{air} A	Intensity	ν_{vac} cm^{-1}	Term combination
10828. 04	1	9232. 76	$a\ ^5F_4 - z\ ^5G_5^0$
10820. 31	5	9239. 35	$x\ ^3F_3^0 - e\ ^3G_4$
10817. 35	5*b*	9241. 88	$x\ ^5D_2^0 - f\ ^5F_2$ $x\ ^5D_1^0 - f\ ^5F_1$
10806. 03	2	9251. 56	$x\ ^5D_1^0 - f\ ^5F_1$
10793. 65	3	9262. 18	$x\ ^3F_2^0 - e\ ^3G_3$
10781. 34	3	9272. 75	$b\ ^3P_2 - x\ ^3D_2^0$
10774. 92	12	9278. 27	$x\ ^5D_0^0 - f\ ^5F_1$ $a\ ^5F_2 - z\ ^5G_2^0$
10756. 90	5	9293. 82	$b\ ^3P_1 - x\ ^3D_1^0$ $x\ ^5D_1^0 - f\ ^5F_2$
10751. 80	1	9298. 23	
10747. 62	1*b*	9301. 84	
10741. 77	7	9306. 91	$x\ ^5D_2^0 - f\ ^5F_3$
10732. 89	8	9314. 60	$a\ ^5F_3 - z\ ^5G_3^0$
10731. 11	6	9316. 15	$x\ ^5D_3^0 - f\ ^5F_4$
10726. 33	18	9320. 30	$a\ ^5F_1 - z\ ^5G_2^0$
10690. 88	1	9351. 20	
10689. 52	15	9352. 39	$x\ ^5D_4^0 - f\ ^5F_5$
10677. 04	10	9363. 33	$a\ ^5F_4 - z\ ^5G_4^0$
10661. 61	20	9376. 88	$a\ ^5F_2 - z\ ^5G_3^0$
10646. 68	3	9390. 91	
10627. 67	1	9406. 82	$z\ ^3S_1^0 - e'\ ^3P_1$
10607. 78	10	9424. 46	$a\ ^5F_5 - z\ ^5G_5^0$
10594. 90	2	9435. 92	$y\ ^5G_5^0 - e\ ^5F_4$
10591. 69	1	9438. 78	$y\ ^5G_4^0 - e\ ^5F_3$
10589. 75	2	9440. 51	$y\ ^5G_6^0 - e\ ^5F_5$
10584. 66	25	9445. 05	$a\ ^5F_3 - z\ ^5G_4^0$
10565. 97	5	9461. 76	$a\ ^3H_4 - y\ ^3G_5^0$
10553. 02	8	9473. 37	$a\ ^3H_5 - y\ ^3G_4^0$
10551. 81	3	9474. 45	$a\ ^3G_5 - z\ ^1G_4^0$
10548. 64	2*b*	9477. 30	
10496. 14	30	9524. 71	$a\ ^5F_4 - z\ ^5G_5^0$
10460. 07	10	9557. 55	$a\ ^3H_6 - y\ ^3G_5^0$
10453. 42	2*b*	9563. 63	
10415. 53	2*b*	9598. 42	
10400. 84	1	9611. 97	$x\ ^3G_3^0 - f\ ^3F_2$
10398. 93	1	9613. 74	$z\ ^3S_1^0 - e'\ ^3P_2$
10396. 85	25	9615. 66	$a\ ^5F_5 - z\ ^5G_6^0$
10338. 59	2*b*	9669. 85	$x\ ^3G_4^0 - f\ ^3F_3$
10257. 30	3*b*	9746. 48	$x\ ^3G_5^0 - f\ ^3F_4$
10189. 26	3	9811. 57	$b\ ^3F_4 - z\ ^3G_4^0$
10179. 92	3*b*	9820. 48	$w\ ^3G_5^0 - f\ ^3G_5$
10170. 60	3	9829. 57	$b\ ^3F_3 - z\ ^3G_3^0$
10147. 09	4	9852. 34	$w\ ^3G_3^0 - f\ ^3G_3$
10145. 48	8	9853. 91	
10120. 90	10	9877. 84	$a\ ^3D_3 - x\ ^3D_2^0$
10119. 20	3	9879. 50	$w\ ^3G_4^0 - f\ ^3G_4$

3. CARBON

The lines of the neutral carbon atom given in table 3 were measured to obtain improved wave lengths for use in identification of infrared solar lines. These carbon lines were previously known, partly from the work of Ryde,[7] but mainly from that of Ingram,[8] who gave the classifications. However, the observations of these investigators yielded only approximate values for the wave lengths. Edlén [9] has recently given more accurate measurements. In the present work, the wave lengths are derived from spectrograms taken in the first order of the large concave grating ruled with 20,000 lines per inch and having a dispersion of 3.6 A/mm. The light source was a condensed discharge through a Geissler tube containing CO_2 at a pressure of approximately 5 mm. These lines are also observable in the spectrum of an arc between graphite electrodes, but they are broadened in the arc and are affected by blending with lines belonging to the bands with heads at 9140 and 10925 A. The former of these bands was first recorded photographically by Asundi and Ryde,[10] who tentatively designated it as the (0,0) band of the $^2\Pi \rightarrow {}^2\Sigma$ system of CN. Subsequently, it was photographed with higher dispersion by Parker,[11] who has given an analysis of it. The band at 10925 A is new and is apparently a member of the same system as the one at 9140 A. It is traceable on our plates out to 11800 A and is accompanied by a much fainter band with head at 10872 A.

TABLE 3.—*Wave lengths in the infrared spectrum of carbon*

λ_{air} A	Intensity	ν_{vac} cm^{-1}	Term combination
11330. 36	1	8823. 43	$3p\ {}^1P_1 - 3d\ {}^1D_2$
10729. 59	8	9317. 47	$3s\ {}^3P_2 - 3p\ {}^3D_2$
10707. 44	8	9336. 75	$3s\ {}^3P_1 - 3p\ {}^3D_1$
10691. 36	50	9350. 78	$3s\ {}^3P_2 - 3p\ {}^3D_3$
10685. 44	10	9355. 97	$3s\ {}^3P_0 - 3p\ {}^3D_1$
10683. 18	25	9357. 95	$3s\ {}^3P_1 - 3p\ {}^3D_2$
9658. 49	2	10350. 75	$3s\ {}^3P_2 - 3p\ {}^3S_1$
9620. 86	1	10391. 23	$3s\ {}^3P_1 - 3p\ {}^3S_1$
9603. 09	0	10410. 46	$3s\ {}^3P_0 - 3p\ {}^3S_1$
9405. 77	20	10628. 86	$3s\ {}^1P_1 - 3p\ {}^1D_2$
9111. 85	10	10971. 71	$3s\ {}^3P_2 - 3p\ {}^3P_1$
9094. 89	25	10992. 17	$3s\ {}^3P_2 - 3p\ {}^3P_2$
9088. 57	8	10999. 81	$3s\ {}^3P_1 - 3p\ {}^3P_0$
9078. 32	6	11012. 23	$3s\ {}^3P_1 - 3p\ {}^3P_1$
9062. 53	10	11031. 42	$3s\ {}^3P_0 - 3p\ {}^3P_1$
9061. 48	15	11032. 70	$3s\ {}^3P_1 - 3p\ {}^3P_2$
8335. 19	10	11994. 03	$3s\ {}^1P_1 - 3p\ {}^1S_0$

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CONSISTENCY OF EIGHT TYPES OF VITREOUS ENAMEL FRITS AT AND NEAR FIRING TEMPERATURES

By William N. Harrison, Robert E. Stephens, and Stephen M. Shelton

ABSTRACT

The consistency of eight vitreous enamel frits, representing eight commercial types, was studied at and near the firing temperatures by means of a small rotation viscometer. The results are expressed in terms of viscosity for the frits which behaved as simple viscous liquids and apparent viscosity for those not behaving as viscous liquids. Comparisons are made at constant torque in the apparatus, and the effect of variations in temperature and variations in type of frit are reported. Also, for individual enamel frits, the effect of varying the speed of rotation at different constant temperatures is shown graphically.

CONTENTS

	Page
I. Introduction	39
II. Apparatus, procedure, and description of enamel frits	40
1. Description of apparatus	40
2. Calibration of apparatus	42
3. Procedure	42
4. Description of enamel frits	43
III. Results and discussion	45
1. Frits of simple viscous consistency	45
2. Frits of complex consistency	46
3. Frits of erratic consistency	50
4. Discussion	52
IV. Summary of findings	54

I. INTRODUCTION

The investigation reported in this paper represents the first work on a somewhat extensive program of research on vitreous enamels. This program was planned with the cooperation of an advisory committee of men active in the industrial and educational aspects of enameling.[1] The first item on this program was the determination of the important properties of eight vitreous enamel frits, which were selected with some care as representative of eight commercial types. This paper reports the results of a study conducted at this Bureau on the consistency of the eight frits at and near their firing temperatures. No additions of clay, opacifiers, or other materials were made to these frits. Such additions to the frits would undoubtedly change their properties, but a study of these effects was considered outside the scope of the present investigation.

[1] For a report of the advisory committee meeting and the names of the members, see Technical News Bulletin of the National Bureau of Standards 213 (Jan. 1935).

The members of the advisory committee having industrial connections assisted greatly in the work by supplying materials and preparing the frits in lots of several hundred pounds, so that these will be available throughout the entire series of studies still to be made. The authors acknowledge the invaluable help which these men and the other members of the advisory committee are contributing to this work.

The importance of knowing the consistency of enamels at or near firing temperatures is attested by the fact that a number of empirical tests are in use, often performed on the frits without mill additions, which are intended to indicate the flow characteristics of enamels during firing. Results obtained by several of these methods were compared in a previous paper.[2] In the present investigation, data were obtained which permitted the expression of results in terms of viscosity, or for enamels which do not behave as viscous liquids, in terms of apparent viscosity.

II. APPARATUS, PROCEDURE, AND DESCRIPTION OF ENAMEL FRITS

1. DESCRIPTION OF APPARATUS

A deflection-type rotation viscometer was chosen as the most suitable instrument. The viscometer was designed to contain only about 3 ml of material in order to facilitate bringing the entire sample to a steady temperature, with minimum temperature gradient, in a short time. Thus any change in composition and consistency of the sample through the necessity of long standing at firing temperatures was materially reduced.

A diagram of the apparatus is shown in figure 1. The cup and spindle are made of platinum containing 5 percent of iridium. The cup is 2 mm thick, 13 mm inside diameter, and 30 mm inside height. The hollow spindle, 6 mm outside diameter and 1.5 mm thick, was immersed during test to 5 mm from the bottom of the cup. The cup is suspended from above instead of being supported from below, so that the thermal expansion of the respective supporting elements, which are Nichrome in the case of both the cup and the spindle, will act in the same direction and tend to avoid a change in the depth of immersion of the spindle with temperature. The Nichrome cylinder supporting the cup is set in ball bearings and is revolved by means of a small, variable-speed electric motor with worm gear and pulley (not shown in fig. 1) acting through belts and a double set of multiple pulley wheels. The variation in motor speed and in the reduction ratio of the pulley system permitted a wide range of speeds of rotation for the cup during the tests.

The inner cylinder assembly is suspended by a piece of tungsten wire, selected because of the low elastic hysteresis of this material. During a test this wire is twisted by the torque transmitted from the revolving cup to the spindle by the test material. The amount of twist is measured by means of a mirror and scale. The scale and reading telescope are not shown in figure 1.

[2] W. N. Harrison and B. J. Sweo. *Some fusion properties of ground-coat enamels as influenced by composition.* BS J. Research 10, 189 (1933) RP524.

The temperature of the specimen during the test is measured with a platinum to platinum-rhodium thermocouple, with its junction in the spindle at the center of the sample and its lead wires emerging from the

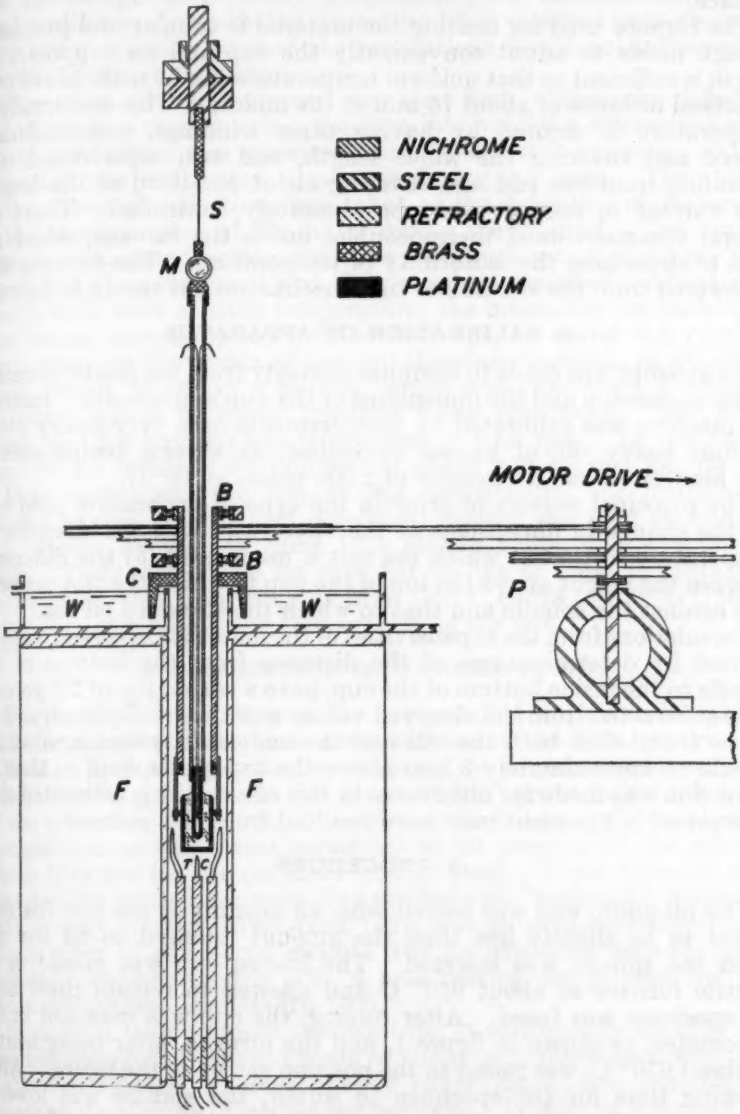

FIGURE 1.—*Schematic diagram of the viscometer.*

S, suspension wire (tungsten).
M, mirror.
B, ball bearings.
W, water.
C, cooling flange.
F, furnace.
TC, thermocouples.
P, pulleys.

supporting cylinder near the mirror. The temperature of the cold junction was maintained at 0° C and the electromotive force was read to ±0.01 mv. The rising of heat toward the torque wire during test is retarded by a flat metal dish containing water, which is in contact with

the top of the furnace. A brass flange, attached to the outer Nichrome cylinder, conducts heat from it into the water, which is cooled by evaporation. The entire viscometer is mounted independently of the furnace.

The furnace used for melting the material is tubular and just large enough inside to admit conveniently the cup and its support. Its length is sufficient so that uniform temperature can be maintained over a vertical distance of about 75 mm at the middle. This uniformity of temperature is secured by having three windings, one uniformly spaced and covering the whole length, and two tapered-end coils extending from one end and covering about one-third of the length. The current in each coil can be separately controlled. There are several chromel-alumel thermocouples inside the furnace, which are used to determine the uniformity of temperature. The furnace may be lowered from the viscometer by a mechanism not shown in figure 1.

2. CALIBRATION OF APPARATUS

No attempt was made to compute viscosity from the elastic constant of the suspension and the dimensions of the cup and spindle. Instead, the machine was calibrated by measurements on a very heavy and a medium heavy oil, of known viscosities, at several temperatures.[3] The heavier oil had a viscosity of 2,090 poises at 15° C.

The principal sources of error in the type of calibration used are: (*a*) the change in dimensions of the viscometer with its elevation in temperature to that at which the test is made, and (*b*) the difference between the height above the top of the cup to which the test material rose against the spindle and that to which the standard oil rose.

Calculations from the expansivities of the materials involved, supplemented by determinations of the distance from the bottom of the spindle to the inside bottom of the cup, gave a correction of 2.7 percent to be subtracted from the observed values at 800° C. By observation, it was found that both the oils and the molten frits rose against the spindle to approximately 3 mm above the top of the cup, so that no correction was made for differences in this effect. It is estimated that an error of ±1 percent may have resulted from this source.[4]

3. PROCEDURE

The platinum cup was loaded with an amount of the test frit estimated to be slightly less than the amount required to fill the cup when the spindle was inserted. The loaded cup was placed in an electric furnace at about 950° C and allowed to remain there until the specimen was fused. After cooling, the cup was mounted in the viscometer, as shown in figure 1, and the furnace, after being heated to about 950° C, was raised to the position shown in the figure. After allowing time for the specimen to soften, the spindle was lowered into position by a screw mechanism. The furnace was then lowered,

[3] The viscosity of the standard oils was determined by R. C. Hardy, of the lubrication and liquid fuels section of the National Bureau of Standards.

[4] The ratios of surface tension to density for the oils and enamel frits would indicate that, at equilibrium conditions in a large enough container, the molten frits would rise against the spindle to a level considerably higher than the oils. Under the conditions of test, however, no substantial difference was observed.

and a sufficient number of grains of frit added to bring the outer rim of the molten material level with the top of the cup, the meniscus sloping upward to the spindle. With the furnace again in position and the sample at a steady temperature, the thermocouple within the spindle was disconnected where the leads emerged from the small supporting cylinder, so that the connections would not influence the amount of mirror deflection.

The lowest viscometer speed was used first. When the deflection had attained a steady value, the time interval for a convenient number of revolutions was measured (usually about 2 minutes), and the deflection was read every 10 seconds during this time. The average of the observed deflections was taken as the deflection corresponding to the average speed of the motor during the interval. The temperature was observed before and after each such set of readings. The speed was then increased and the procedure repeated. About eight speeds were used at each temperature, the maximum for each specimen being approximately 0.07 to 0.08 rps, or about 4.5 rpm. A given point on the inside of the cup therefore traveled, at maximum speed, about 20 cm in a minute, which was considered a sufficient maximum speed to cover practical firing conditions. The lowest speed used for any frit was 0.0005 rps, or 0.03 rpm. In this case, a point on the inside of the cup moved about 0.13 cm in 1 minute.

After completing the test at one temperature, the furnace was allowed to cool about 50° C, a reduced current was then applied, the temperature allowed to come to a steady value, and another test made. Tests were made on each frit at five or more temperatures, the range covered being roughly from 100° C above to 100° C (180° F) below the estimated firing temperature of the frit.

4. DESCRIPTION OF ENAMEL FRITS

The batch compositions of the frits studied are given in table 1, and the calculated chemical compositions of the frits are given in table 2. Each composition is supposed to be representative of its type. "Soft" ground-coat frit 1 and "hard" ground-coat frit 11 are of the types frequently mixed to form a two-frit ground coat, the soft composition usually constituting 20 to 40 percent of the mixture. These frits are for use on sheet iron or steel. Three types of cover coat for the same base were also studied: an "ordinary" white coat (25), a very opaque cover coat (35), and an acid-resisting frit (6). Three types of cover-coat enamel frits for cast iron were studied: a high-lead wet-process frit (72), a lead-bearing dry-process frit (85), and a dry-process leadless frit (65).

In enamel frits at room temperature, it can usually be seen with the microscope that ground coats of the type studied have very little suspended matter, whereas opaque cover coats have variable but substantial amounts of suspended particles. It is to be expected that a similar difference exists, at least to some degree, in the range of firing temperatures. Those frits containing considerable amounts of suspended matter at the temperatures of test would not be expected to behave as simple viscous liquids.

TABLE 1.—*Batch composition of enamel frits*

Ingredients	Soft ground coat	Hard ground coat	Ordinary white	Very opaque white	Acid-resisting white	Cast iron wet process (lead) [1]	Cast iron dry process (lead)	Cast iron dry process (leadless)
	Frit 1	Frit 11	Frit 25	Frit 35	Frit 6	Frit 72	Frit 85	Frit 66
Feldspar	31.00	31.00	22.80	17.60	9.50	18.72	32.44	31.66
Flint	11.40	18.00	21.13	23.47	39.00	9.13		
Borax	37.10	37.10	23.07	22.88	18.00	18.82	25.27	27.87
Soda ash	5.90	5.90	6.34	6.70	10.00		2.70	1.72
Soda nitre	3.80	3.80	2.96	2.93	3.00	3.35	2.95	2.87
Fluorspar	9.00	3.00	3.38	2.51	1.50	5.10	8.42	8.19
Cryolite			10.14	8.38		3.00		
Zinc oxide			3.38	2.93			6.74	7.78
Sodium antimonate			6.76	12.58	9.50		9.26	9.42
Sodium silicofluoride					5.00			
Lead oxide						36.10	8.42	
Bone ash					1.50	3.78		
Titanium oxide					3.00			
Barium carbonate						2.00	3.79	10.57
Cobalt oxide	0.50	0.50						
Nickel oxide	.40	.60						
Manganese oxide	.90	1.10						
Total	100.00	101.00	99.96	99.98	100.00	100.00	99.99	99.98

[1] Not opaque—for use with color stain in mill batch.

TABLE 2.—*Chemical composition of enamel frits, as calculated from batch weight*

[Feldspar analysis known. All other batch materials considered as pure]

Ingredients	Soft ground coat	Hard ground coat	Ordinary white	Very opaque white	Acid-resisting white	Cast iron wet process (lead)	Cast iron dry process (lead)	Cast iron dry process (leadless)
	Frit 1	Frit 11	Frit 25	Frit 35	Frit 6	Frit 72	Frit 85	Frit 66
SiO_2	40.9	49.2	42.1	45.4	55.1	24.2	25.6	25.3
TiO_2					3.5			
Al_2O_3	7.7	7.7	8.0	6.4	2.2	4.9	7.6	7.5
Fe_2O_3	tr	tr	tr	tr	tr	tr	tr	tr
B_2O_3	17.5	17.4	9.8	9.7	7.7	7.8	11.1	12.5
CaO	8.4	2.9	2.9	2.2	2.3	6.5	7.4	7.3
BaO						1.7	3.5	10.0
NiO	0.5	0.7						
CoO	.6	.6						
MnO_2	1.2	1.4						
ZnO			3.9	3.4			8.1	9.5
PbO						40.7	10.1	
K_2O	4.5	4.5	3.0	2.3	2.1	2.4	4.4	4.4
Na_2O	15.3	15.2	17.3	17.5	15.7	7.0	9.9	11.1
F_2*	3.5	0.4	6.4	0.8	2.2	2.8	3.0	2.9
Sb_2O_3			6.6	12.4	8.4		9.3	9.6
P_2O_5					0.8	2.0		
Total	100.1	100.0	100.0	100.1	100.0	100.0	100.0	100.1

* The percentage of F_2 which was lost in smelting was computed from data forwarded by Robert B. Schaal, then of Roberts and Mander Stove Co.

III. RESULTS AND DISCUSSION

From the data obtained on each frit a graph was made showing the relation of viscometer deflection to speed of rotation for each temperature at which the frit was tested. In these graphs, the actual viscometer deflections are of course of little significance since they depend on the dimensions of the apparatus and are therefore treated as arbitrary units. The property which is of fundamental significance is the viscosity (and to a lesser extent the apparent viscosity). This quantity is given on the speed-deflection charts, the unit being the poise.

1. FRITS OF SIMPLE VISCOUS CONSISTENCY

Frits 1 and 11, the graphs for which are shown in figures 2 and 3, respectively, behaved as viscous liquids, the speed-deflection curves being straight lines passing through the origin. Each such curve is

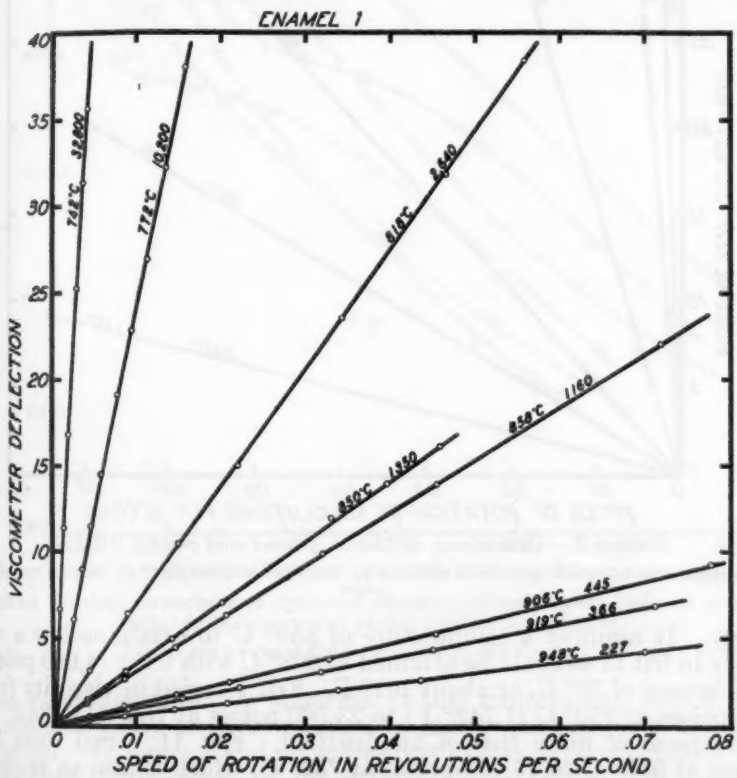

FIGURE 2.—*Consistency of "soft" ground-coat enamel frit 1.*

Linear relation between viscometer deflection and speed of rotation indicates simple viscous consistency. The numbers following "° C" indicate viscosity in poises.

labeled in these figures with the temperature and the viscosity in poises. At temperatures between the indicated limits the viscosities which are not shown can be read by interpolation on the graphs, along any straight line parallel to an ordinate.

In figure 4 the logarithms of the viscosities (in poises) are plotted against temperature for several enamel frits, including 1 and 11. Although the curves for these ground coats are roughly parallel, it is seen that frit 1 increased in viscosity with lowering temperature more rapidly than frit 11. At 850° C frit 11 was over 3.5 times as viscous as frit 1, the viscosities being 5,000 poises and 1,430 poises, respec-

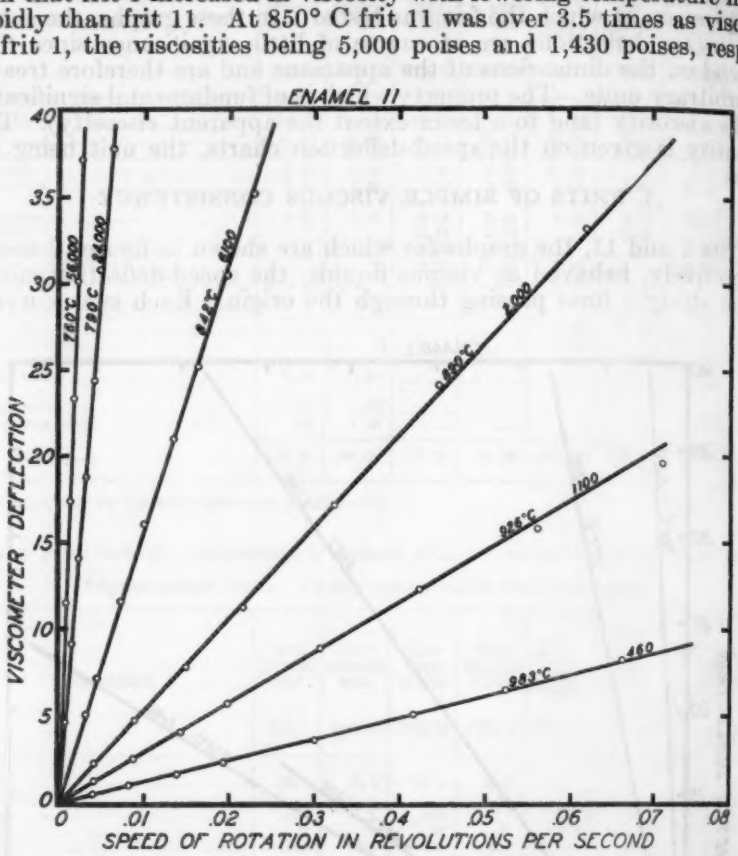

FIGURE 3.—*Consistency of "hard" ground-coat enamel frit 11.*

The straight lines indicate simple viscous consistency. The numbers following "° C" indicate viscosity in poises.

tively. It required a temperature of 859° C to attain as low a viscosity in frit 11 as could be attained at 803° C with frit 1 (4,000 poises) a difference of 56° C, or about 101° F. Frit 1 varied in viscosity from 216 poises at 950° C (1,742° F) to 23,000 poises at 750° C (1,382° F), an increase of more than a hundredfold. Frit 11 varied from 725 poises at 950° C to 75,000 poises at 750° C, which is also an increase of over a hundredfold.

2. FRITS OF COMPLEX CONSISTENCY

The speed-deflection curves for acid-resisting cover-coat frit 6, shown in figure 5, are so nearly straight at several temperatures that no curvature could be detected with certainty. However, in the results obtained at 893° C, and to a greater extent in those obtained at 934° C, a definite curvature is apparent, indicating that the ma-

terial is not a simple viscous liquid. Inasmuch as there is no evidence that any of these curves fail to pass through the origin, it may be said that at these temperatures frit 6 behaved as a complex liquid, sometimes called a non-Newtonian liquid.[5] Each curve in figure 5 has been labeled with a number indicating the average apparent viscosity.

Figure 6 shows the data for ordinary sheet-iron cover coat 25. All of the speed-deflection lines in this graph are definitely curved except that obtained at 750° C, and the nature of the entire chart suggests

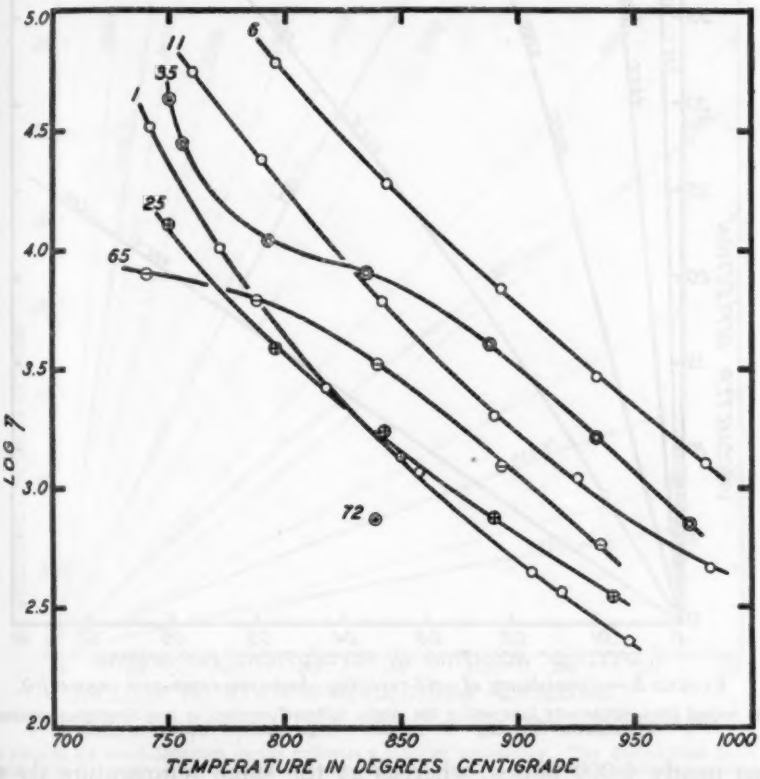

FIGURE 4.—*Log viscosity and apparent viscosity of six enamel frits at constant torque in the apparatus plotted against temperature.*

A single value at 839° C for enamel frit 72 is shown.

that curvature would be apparent at this temperature, too, if rates of shear as great as those reached at higher temperatures had been attained. In figure 6 and all succeeding figures, straight dashed lines have been superimposed on the charts. These dashed lines show the positions on the graphs corresponding to various viscosities. Wherever the curves cross these lines, the apparent viscosity of the sample at the indicated temperature and speed of rotation was equal to that indicated by the dashed line. The apparent viscosity for any point

[5] For pertinent definitions, see Proc. Am. Soc. Testing Materials, part 1, **34**, 1245 (1934). With the method of plotting adopted, a straight speed-deflection line passing through the origin denotes a simple viscous liquid, while a curved line, also passing through the origin, denotes a complex or non-Newtonian liquid.

on any data curve can be read by simple interpolation between two dashed lines, in a direction parallel to the ordinate.

Very opaque frit 35, the results for which are shown in figure 7, displayed a marked departure from simple viscous consistency. For example, at 887° C the apparent viscosity at a speed of 0.0028 rps

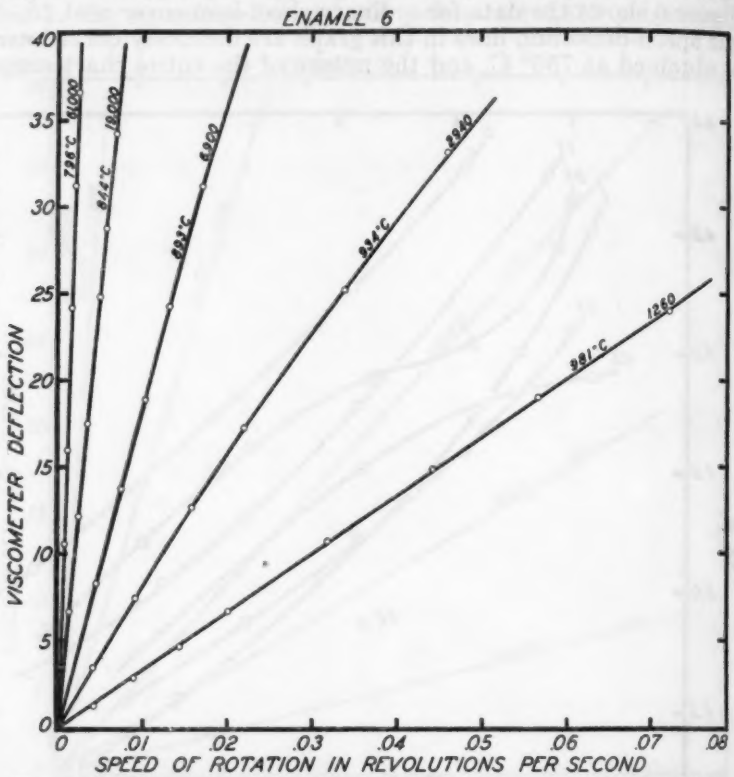

FIGURE 5.—*Consistency of acid-resisting sheet-iron cover-coat enamel frit.*

The curved lines, apparently intersecting the origin, indicate complex, or non-Newtonian consistency. The numbers following "°C" indicate average apparent viscosity in poises.

was nearly 6,000 poises, whereas at the same temperature the apparent viscosity at 0.060 rps was less than 2,000 poises.

Dry-process leadless frit 65, data for which are shown in figure 8, gave speed-deflection lines of even greater curvature than those of frit 35. At 936° C, for example the apparent viscosity at a speed of 0.0042 rps was 2,600 poises, whereas at 0.0696 rps it was only 536 poises, or approximately one-fifth as much. Nevertheless, the results were quite systematic, and gave no indication that any of the curves failed to pass through the origin.

Comparison of the apparent viscosities of frits 6, 25, 35, and 65 at stated temperatures must be made either at constant speed of rotation or at constant torque. Since, in practice, the force tending to make the enamel flow during firing would presumably be more nearly constant than the rate of flow, comparisons at constant torque were considered preferable. In figure 4 the apparent viscosities of these frits, at a viscometer deflection of 10 units, is plotted against temperature together with the viscosities of ground coats 1 and 11.

Figure 4 shows that acid-resisting sheet-iron frit 6 had the highest resistance to flow of all the frits shown. Its curve for log viscosity against temperature is almost parallel to that for ground-coat frit 11. At equal temperatures frit 6 was, however, about 3 times as resistant to flow as ground coat 11, and about 10 times as resistant as ground coat 1.

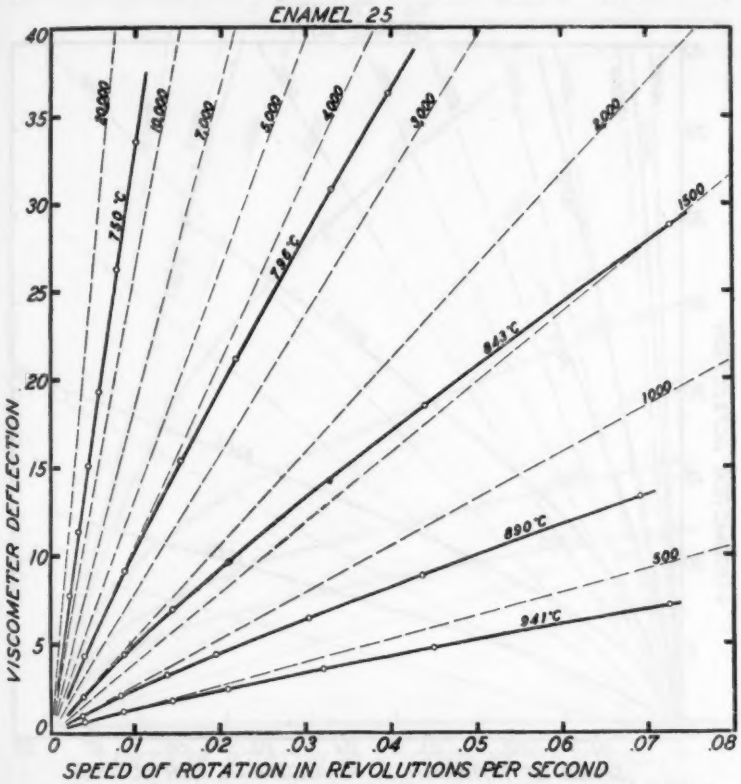

FIGURE 6.—*Consistency of "ordinary" sheet-iron cover-coat enamel frit.*

The shape of the speed-deflection curves indicates a complex consistency. The dashed lines show the positions on the graph corresponding to the viscosities, in poises, indicated by the adjacent numbers.

The ordinary sheet-iron cover coat 25 was about as resistant to flow between 800 and 850° C as ground coat 1, but below this temperature range it was more fluid, and above, less fluid than the ground coat.

The consistency of the very opaque sheet-iron cover coat 35 was so complex that a graph of apparent viscosity, at any selected torque, against temperature has questionable significance. Figure 4 does show, however, that the apparent viscosity of this frit is within the range found for other enamel frits, and is in the high-viscosity part of this range, between the temperatures of 850 and 950° C, within which zone it probably would be fired.

The significance of the curve relating log apparent viscosity of enamel frit 65 to temperature, at constant torque, is also questionable. However, this curve indicates that the apparent viscosity was in the lower part of the range covered by the entire series of frits, and appears

similar in trend to the curve for frit 35, but shows equal apparent viscosity at about 60° C (108° F) lower than frit 35. There are no data to show whether the curve for frit 65 would curve upward at temperatures below 740° C, thus carrying through its parallelism to the curve for frit 35. This temperature was considered safely below the probable firing temperature of actual practice.

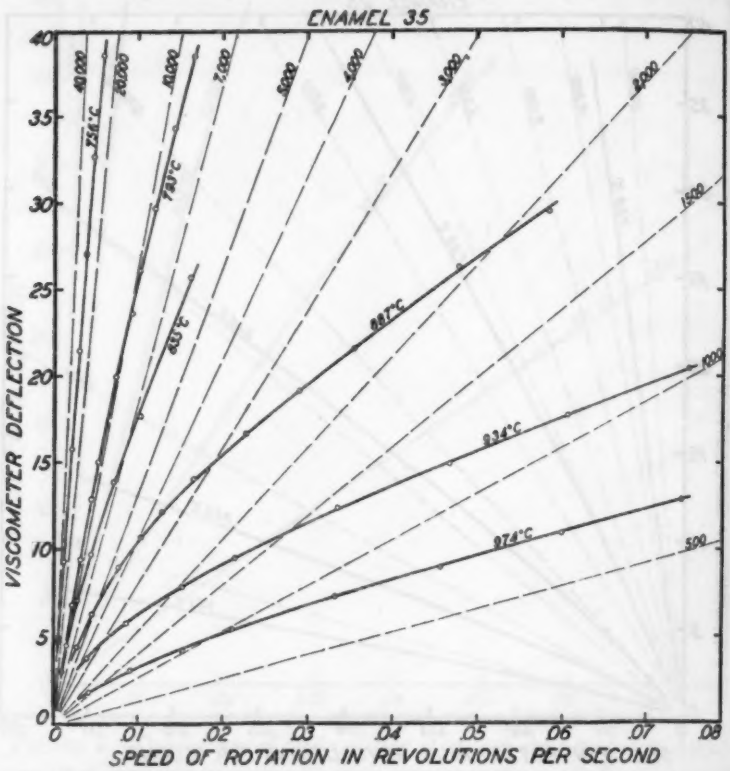

FIGURE 7.—*Consistency of a very opaque enamel frit for sheet iron.*

The marked curvature of the speed-deflection curves, which appear to pass through the origin, indicates a complex consistency. The dashed lines show the positions on the graph corresponding to the viscosities, in poises, indicated by the adjacent numbers.

3. FRITS OF ERRATIC CONSISTENCY

Frit 72, a high-lead composition for use with added stains to produce various colors in the wet-process enameling of cast iron, and number 85, a lead-bearing dry-process frit, were found to have consistencies which can well be described as erratic. These are the only lead-bearing frits studied. The data are shown in figures 9 and 10, respectively. It may be seen in figure 9 that frit 72, at 780° C, decreased gradually in apparent viscosity with increased speed of rotation up to 0.0046 rps. Further increase of speed up to 0.0058 rps gave no increase in deflection. Additional increase in speed gave a more rapid decrease in apparent viscosity than occurred at lower speeds, followed by still more rapid decrease with higher speeds. Although not exactly reproduced, the general shape of this curve was

established by several tests at approximately this temperature. The kink in the curve, which occurred at speeds around 0.005 rps, did not appear to be caused by experimental error. The first data in figure 9 were taken at 927° C and the last at 930° C. It is seen that the latter curve is smoother and is more definitely pointed toward the origin.

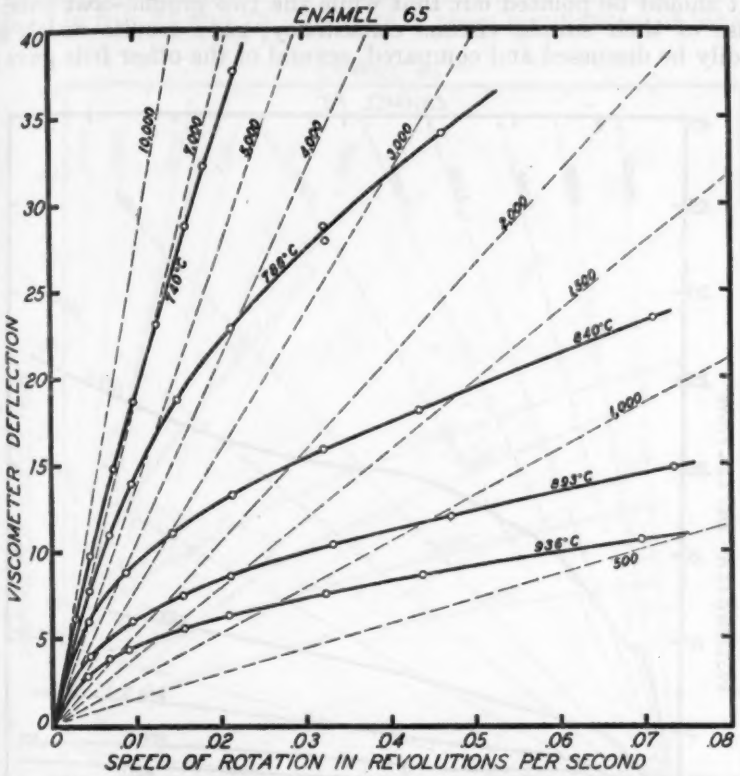

FIGURE 8.—*Consistency of a leadless dry-process enamel frit.*

The sharply curved speed-deflection lines indicate distinctly complex consistency. The dashed lines show positions on the graph corresponding to the viscosities, in poises, indicated by the adjacent numbers.

Figure 10 shows not only the erratic nature of the relation between temperature, speed of rotation, and apparent viscosity of frit 85, but also its instability under the conditions of test. The data were taken in order of decreasing temperature except that after the test at 736° C a second test at 835° C was made. The second test at this temperature showed lower apparent viscosities and a speed-deflection curve much more typical of other frits than that obtained in the first test at 835° C. This was the only frit for which curves obtained at substantially different temperatures actually crossed.

The data obtained on these two frits are not suitable, on the whole, for representation in figure 4. Nevertheless, one point from figure 9, namely, the apparent viscosity of frit 72 at 839° C and at a deflection of 10 units on the viscometer, has been placed in figure 4. The apparent viscosity of this composition, under the indicated conditions, is less than half that of frits 1 and 25, which are next higher. The

average of the two curves for frit 85 at 835° C and 10 units of viscometer deflection corresponds to an apparent viscosity somewhat greater than that of frit 65 under the same conditions.

4. DISCUSSION

It should be pointed out that while the two ground-coat frits, because of their simple viscous consistency, gave results which may readily be discussed and compared, several of the other frits gave the

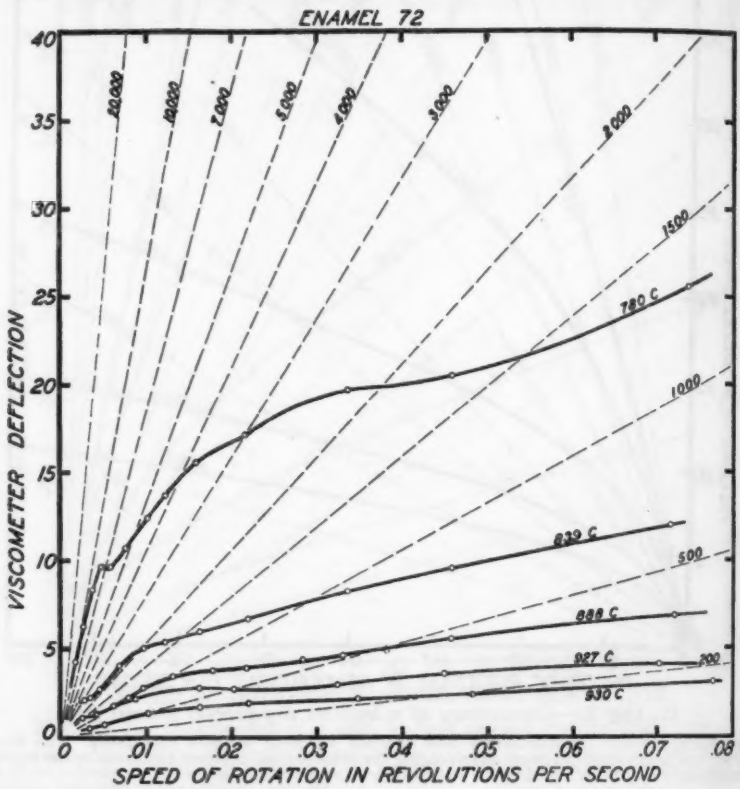

FIGURE 9.—*Consistency of a high-lead wet-process cast-iron enamel frit.*

The curves show marked deviation from simple viscous consistency, and the one for 780° C shows also an erratic shape near 7,000 poises, apparent viscosity. The dashed lines show positions on the graph corresponding to the viscosities, in poises, indicated by the adjacent numbers.

reported results only when they were tested in the particular manner described. Thus, frit 35 gave the results shown in figure 7 when the viscometer speeds were successively increased at given temperatures, but when returned to a given speed of rotation following a test at a higher speed, this frit gave first a smaller and later a greater deflection than the original apparent equilibrium value. This phenomenon may be a manifestation of thixotropy.[6] Frits 6, 25, 65, 72, and 85 behaved, in part, like frit 35, that is, when retested at a given speed of rotation

[6] Thixotropy may be defined as the tendency of a material to form a relatively stiff structure when not disturbed, which breaks down and gives place to a more fluid consistency under agitation. See E. L. McMillen, Effect of thixotropy on plastic measurements, J. Rheology 3, 185 (1932).

after a test at a higher speed, they gave different deflections than originally. It was thought that the procedure used, namely, to obtain values at successively increased speeds for any one temperature, was the one likely to yield values for consistency which would prevail in practice during the firing process.

Frit 85 appeared distinctly unstable, and some instability was also noticed in frits 35 and 72. In spite of these peculiarities of behavior

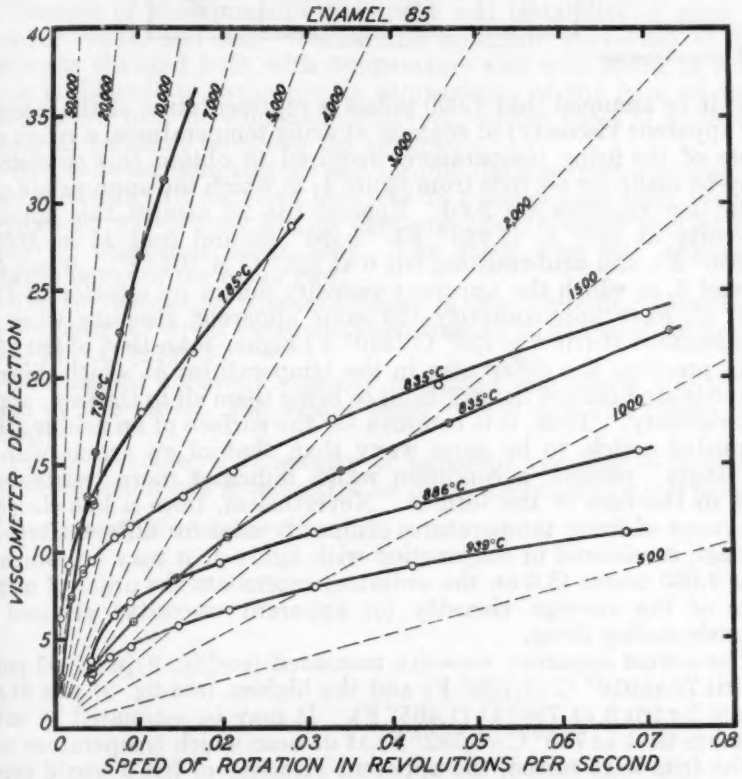

FIGURE 10.—*Consistency of a lead-bearing dry-process enamel frit.*

The shape of the curves indicates marked deviation from simple viscous consistency. The facts that some of the curves cross each other, and that two tests at 835° C taken at different times on the same sample did not agree, indicate an unstable consistency. The dashed lines show the positions on the graph corresponding to the viscosities, in poises, indicated by the adjacent numbers.

and the complex consistency of the cover-coat frits, some interesting comparisons may be made.

It so happens that the temperature 839° C (1,542° F) (which is the only temperature given for frit 72 in fig. 4), is within the usual range of firing temperatures of enamels, and a comparison of the different frits, under constant torque, at this temperature, is of interest. The figures are given in table 3.

It is seen in table 3 that under the indicated conditions the resistance to flow of acid-resisting frit 6 is over 28 times as great as that of frit 72 and over 12 times that of frit 25.

TABLE 3.—*Apparent viscosities of eight enamel frits under a chosen torque at 839° C (1,542° F)*

Frit	Apparent viscosity	Frit	Apparent viscosity
	Poises		*Poises*
72	750	85	* 4,140
11	1,660	11	6,460
25	1,740	35	7,760
65	3,390	6	21,380

* Estimated average.

If it be assumed that 4,000 poises is representative of the viscosity (or apparent viscosity) of enamels at firing temperatures, a rough estimate of the firing temperatures required to obtain this consistency may be made for six frits from figure 4, in which the appropriate ordinate (log viscosity) is 3.60. Enamel frit 25 attains this apparent viscosity at 795° C (1,463° F), "hard" ground coat 11 at 860° C (1,580° F), and acid-resisting frit 6 at 928° C (1,702° F). Thus, frits 25 and 6, in which the apparent viscosity differs by a factor of 12 at 839° C, have approximately the same apparent viscosity when the temperature of frit 6 is 133° C (239° F) higher than that of frit 25.

In practice, the differences in the temperatures at which different enamels are fired are not sufficient to bring them all to the same apparent viscosity. Thus, it is common for the surface of an acid-resisting enameled article to be more wavy than that of an article with an "ordinary" enamel, a condition which indicates more resistance to flow in the case of the former. Nevertheless, from a knowledge of the range of firing temperatures ordinarily used for different types of enamel, considered in conjunction with figure 4, it may be estimated that 4,000 poises (3.6 on the ordinate) represents the order of magnitude of the average viscosity (or apparent viscosity) attained by enamels during firing.

The lowest apparent viscosity measured (see fig. 9) was 155 poises for frit 72 at 930° C (1,706° F) and the highest (see fig. 5) was 61,000 poises for frit 6 at 796° C (1,465° F). It may be estimated by extrapolation that at 750° C (1,382° F), at or near which temperature most of the frits were tested, the apparent viscosity of frit 6 would exceed 200,000 poises.

IV. SUMMARY OF FINDINGS

1. Two sheet-iron ground-coat frits, representing the "hard" and "soft" types often mixed in a single slip, behaved as viscous liquids at and near their firing temperatures.

2. Four types of cover-coat frits behaved, not as viscous liquids, but as complex or non-Newtonian liquids at and near their firing temperatures. The data for these compositions were quite systematic. The types represented in this group were: an "ordinary" cover coat, a very opaque, and an acid-resisting cover coat for sheet iron, and a leadless dry-process frit for cast iron.

3. The two frits containing lead, namely, a dry-process frit with about 10 percent of lead oxide and a wet-process frit for cast iron, containing about 40 percent of lead oxide, did not behave as viscous liquids at the temperatures studied, but as complex liquids exhibiting

erratic behavior, possibly associated with instability and thixotropy. After heating for several hours in the range of firing temperatures, these frits gave speed-deflection curves more in conformity with those of the other compositions studied.

4. For all the frits studied, the change in viscosity or apparent viscosity with temperature was very large, a decrease in temperature from 950 to 750° C (1,742 to 1,382° F) causing as much as a hundredfold increase in the viscosity of some specimens.

5. Because of the apparent thixotropy and instability of some of the cover coats, and also because the apparent viscosities of the cover coats changed both with temperature and with speed of rotation, it is difficult to make simple comparisons of the frits studied. Most of them may be compared, however, on the basis of apparent viscosity at constant torque in the apparatus.

6. At a selected temperature and torque, the apparent viscosity of the acid-resisting frit for sheet iron was 28 times greater than that of the high-lead wet-process frit for cast iron and 12 times that of the "ordinary" sheet-iron cover coat. The other frits had apparent viscosities between the latter two.

7. The two sheet-iron frits mentioned in the preceding paragraph were brought to equal apparent viscosities by a temperature difference of 125° C (225° F).

8. The highest apparent viscosity measured was nearly 400 times as high as the lowest, the values being 61,000 and 155 poises, respectively.

9. On the average, the viscosity or apparent viscosity of enamels under firing conditions is estimated to be on the order of 4,000 poises.

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SOME "SOFT" GLAZES OF LOW THERMAL EXPANSION

By R. F. Geller, E. N. Bunting, and A. S. Creamer

ABSTRACT

Compositions in the ternary field PbO-B_2O_3-SiO_2 were studied as potential glazes both with and without the addition of 5 percent of Al_2O_3. Compositions within a very small field (25 to 40 percent of PbO; 15 to 30 percent of B_2O_3; and 40 to 55 percent of SiO_2) show promise as glazes maturing at temperatures below 1,150° C on talcose bodies of relatively low thermal expansion. Low resistance to solution by weak acids may limit their application to wares which do not come in prolonged contact with food.

CONTENTS

	Page
I. Introduction	57
II. Materials and methods	57
III. Results	59
1. Glasses	59
2. Glazes	63
IV. Discussion and conclusions	65

I. INTRODUCTION

The need for glazes of relatively low maturing temperature and thermal dilatation, occasioned by the development of talcose bodies of similar characteristics,[1] was the incentive for a study of lead borosilicate glasses as a correlary of phase-equilibria determinations in the system PbO-B_2O_3-SiO_2.[2] That glasses of this type might logically be expected to have a low thermal expansion is evident from the expansion coefficients of the constituents.[3] The principal difficulty anticipated was that of low resistance to solution, as has been shown by numerous investigators, more recently by J. H. Koenig.[4]

II. MATERIALS AND METHODS

The materials for preliminary melts were sublimed litharge (PbO) containing 0.02 percent of total detected impurities; boric acid of reagent quality; pulverized quartz (SiO_2) containing 0.02 percent of nonvolatile residue; and Al_2O_3 of 99.95 percent purity. Commercial Pennsylvania "potter's flint", and Georgia kaolin containing 45.3 percent of SiO_2 and 39.1 percent of Al_2O_3 as the source of Al_2O_3, were used in the larger batches, together with the litharge and boric acid described.

[1] R. F. Geller and A. S. Creamer. J. Am. Ceram. Soc. **20**, 137 (1937).
[2] A report of the first phase of this equilibria study has been published (R. F. Geller and E. N. Bunting, The system PbO-B_2O_3, J. Research NBS **18**, (1937) RP995).
[3] F. P. Hall. J. Am. Ceram. Soc. **13**, 182 (1930).
[4] Lead Frits and Fritted Glazes, Ohio State Eng. Exp. Sta. Bul. 95 (1937).

Preliminary melts were fused in platinum and ground in agate mortars. For larger batches, the frit was fused in clay crucibles, using a gas-fired pot furnace, and the glaze mixtures were ground in ball mills to pass a No. 100 sieve. Portions of the preliminary melts were used for determining initial softening temperatures (T_s), linear thermal expansions, and solubility in the powdered form. Portions of the larger batches were used to prepare glazed specimens for determining workability of the slip, maturing temperatures, solubility in situ, and appearance. For convenience, the small preliminary melts will be referred to as glasses (table 1), and the larger batches will be referred to as glazes (table 2). All materials in the glazes not introduced as clay were fritted. The glaze trials were "glost fired" in electrically heated ovens.

TABLE 1.—*Compositions of glasses, softening temperatures, linear thermal expansion, and solubility in the powdered form*

Glass	Preliminary melts, composition G			Softening (T_s)		Expansion, coefficient room temperature to 300° C		Solubility [a]	
	PbO	B_2O_3	SiO_2	G	G, plus 5% of Al_2O_3	G	G, plus 5% of Al_2O_3	G_2	G_2, plus 5% of Al_2O_3
	%	%	%	°C	°C	$\times 10^{-6}$	$\times 10^{-6}$	%	%
1	10.0	9.7	80.3	737		2.1			0
2	9.9	19.5	70.6	685	703	2.8	2.4	5	7
3	19.8	10.0	70.2	735	719	2.5	2.3	tr	0
4	8.9	29.1	62.0	624		3.4		80	91
5	19.8	19.2	61.0	722		3.2		5	34
6	29.5	9.9	60.6	[b]		3.1		9	4
7	8.7	39.7	51.6	535	561	4.7	4.6	100	100
8	19.4	28.9	51.7	655		3.7		68	94
8½	24.8	24.0	51.2	696	658	4.0	3.8	15	99
9	30.1	19.2	50.7	[b]		3.9		43	84
10	39.9	10.0	50.1	[b]	596	4.2	3.7	79	12
11	10.1	48.9	41.0	519		5.4			
12	20.0	39.7	40.3	546	576	4.8	4.4		100
13	30.2	29.3	40.5	[b]	645	4.6	4.3	95	100
14	40.4	19.7	39.9	[b]	643	4.7	4.4	89	98
15	50.2	10.2	39.6	[b]		5.3		90	43
16	10.2	50.5	30.3	413	• 475				
17	20.6	49.0	30.4	489		5.9			
18	30.4	39.0	30.6	554		5.5			
18½	35.3	34.0	30.7		• 616		5.0		100
19	40.2	29.1	30.7	[b]		5.4			
20	50.2	19.9	29.9	[b]		5.3		95	98
21	60.1	10.3	29.6	487	514	7.9	5.9	97	73
22	10.0	68.9	21.1	374		7.8			
23	20.5	59.6	19.9	399		7.1			
24	30.6	49.1	20.3	489		6.3			
25	40.2	39.6	20.2	512		6.0			
26	50.5	29.2	20.3	502		6.2			
27	60.4	19.4	20.2	475		6.3			97
28	69.9	10.2	19.9	460		7.9			94
29	10.2	79.9	9.9	331	443				
30	20.2	69.9	9.9	360		8.9			
31	30.1	59.9	10.0	481	• 478	8.2	6.5		
32	40.2	49.9	9.9	501		6.9			
33	50.2	39.8	10.0	510		6.4			
34	60.1	29.9	10.0	498	496	7.0	6.6		
35	70.1	19.9	10.0	461		7.6			
36	80.0	10.1	9.9	392	409	9.8	9.3		100

[a] Compositions G_2 were prepared using the same batch composition and procedure used in preparing compositions G, but were not analyzed. Solubility values show the PbO extracted, expressed as the percentage of total PbO in the glaze.

[b] Samples crystallized before a normal softening temperature was reached.

• Samples showed slight opalescence after the expansion test.

TABLE 2.—*Compositions of prepared glazes*

Glaze	Chemical				Empirical (molecular ratios)			
	PbO	Al_2O_3	B_2O_3	SiO_2	PbO	Al_2O_3	B_2O_3	SiO_2
	%	%	%	%				
5-9	23.8	5.0	18.8	52.4	1.00	0.49	2.73	9.02
6-9	28.5	5.0	14.1	52.4	1.00	.39	1.66	7.15
8½	24.7	4.9	23.2	47.2	1.00	.43	3.02	7.11
9	28.5	5.0	18.7	47.8	1.00	.40	2.24	6.86
9½	33.6	4.9	14.0	47.5	1.00	.34	1.50	5.70
8-13	23.7	5.0	28.5	42.8	1.00	.52	4.34	7.58
9-13	28.5	4.9	23.1	43.5	1.00	.38	2.67	5.99
9-14	33.3	5.0	18.8	42.9	1.00	.35	1.91	5.29
10-14	38.4	5.0	14.0	42.6	1.00	.28	1.17	4.13
13	28.5	4.8	27.5	39.2	1.00	.37	3.09	5.12
14	38.1	5.0	18.8	38.1	1.00	.29	1.58	3.72

To determine SiO_2 and R_2O_3, 0.5-g samples were fused with Na_2CO_3, dissolved in hot dilute HCl, evaporated almost to dryness, and the moist residue evaporated three times with 10 ml of C_2H_5OH saturated with HCl. This removed the B_2O_3. Silica was then determined in the usual way and the remaining R_2O_3 determined by double precipitation with NH_4OH.

PbO was determined on 0.5-g samples evaporated two or three times with HF and HNO_3 to remove SiO_2 and B_2O_3. HNO_3 was then added and PbO_2 deposited electrolytically. This deposit, after having been dissolved in dilute HNO_3 and C_2H_5OH, was converted to $PbSO_4$ and weighed as such.

B_2O_3 was determined by difference.

Data for establishing the T_g values and coefficients of linear thermal expansion were obtained by the interferometer method using specimens, approximately 3 mm in diameter, which had been fused in platinum capsules.

Resistance of pulverized glass samples to solution was determined by boiling 0.5 to 1.0 g of "through 200, on 325 mesh" material in 200 ml of a 4-percent acetic acid solution. The PbO dissolved was estimated by titrations with ammonium molybdate solution, using tannic acid solution as the external indicator.[5] Specimens having approximately 12 in.^{2} of glazed surface were subjected to the same treatment, but the amount of solution was estimated by precipitating the dissolved lead with H_2S and comparing the darkened solution with standards containing known amounts of Pb, also precipitated with H_2S. In addition, a limited number of tests were made by boiling glazed specimens in a 2-percent solution of potassium carbonate. In preparing glazed specimens for solubility tests, approximately 0.1 g of glaze was applied per square inch of surface.

III. RESULTS

1. GLASSES

Most of the Al_2O_3-free glasses become opalescent or opaque on cooling, only those of low PbO and high (60 percent or more) SiO_2 content, and those of high (60 percent or more) PbO with 20 percent or less of SiO_2 being clear. The addition of 5 percent of Al_2O_3 gave

[5] This is the method used by Koenig. See footnote 4.

clear glasses, except with 60 percent or more of B_2O_3 and 10 percent of PbO.

Values for initial softening temperature (T_s) and for linear thermal expansion are given in table 1 and indicated by iso-lines in figure 1. For the sake of uniformity, average expansion coefficients are given for the range from room temperature to 300° C, because, in many instances, the first "break" or lower critical temperature (T_c) was found below 400° C.

In general, the expansions increase with increasing PbO or B_2O_3 content, but the relation is not linear. At a constant SiO_2 level, the addition of B_2O_3 in place of PbO at first reduces the expansion, becomes a minimum at approximately equal PbO and B_2O_3 content, and then increases again with increase of B_2O_3. For example, at approximately 20 percent of SiO_2 and 20, 40, 60, and 80 percent of PbO, the expansions to 300° C are 19, 16, 17, and 27 μ/cm, respectively. The corresponding average coefficients are 7.1, 6.0, 6.3, and 9.6×10^{-6}. At the 70-percent SiO_2 level, for 10 and 20 percent of PbO, the expansions are 7.6 and 6.8 μ/cm, the corresponding coefficients being 2.8 and 2.5×10^{-6}. The addition of 5 percent of Al_2O_3 to these glasses lowers the expansion by about 10 percent.

The softening point decreases with increasing PbO and B_2O_3 content but not in a linear manner. In most cases, the addition of 5 percent of Al_2O_3 raised the softening point, but in melts 3 and 8½ (table 1) it was lowered, while melts 31 and 34 were practically unaffected.

Solubility values for pulverized samples are given in table 1 and indicated by lines of equal solubility in figure 2. All lead borate glasses (200 to 325 mesh) are completely dissolved by boiling in 4-percent acetic acid, while lead silicates containing over 83 percent of PbO have all the PbO extracted. At 60 percent of PbO and 40 percent of SiO_2, only 9 percent of the PbO is extracted by this treatment and the addition of 5 percent of Al_2O_3 to this composition reduces the extraction to 1 percent. However, the addition of B_2O_3 increases the amount of extractable PbO; for example, at 50 percent of SiO_2, 40 percent of PbO, and 10 percent of B_2O_3, about 75 percent of the PbO is dissolved. At 70 percent of SiO_2, 20 percent of PbO, and 10 percent of B_2O_3, only a trace of PbO is dissolved, whereas at 70 percent of SiO_2, 10 percent of PbO, 20 percent of B_2O_3, about 5 percent of PbO is extracted. The addition of 5 percent of Al_2O_3 has the unexpected effect of increasing the solubility of many compositions.

These values for solubility have significance in a relative sense only, probably because of the effect of surface area, which is very difficult (if not impracticable) to control in pulverized material. Determinations on portions of the same "grind" checked within ±1 percent, but determinations on samples ground at different times varied as much as ±15 percent. The shaded area in the right-hand diagram of figure 2 indicates the field of compositions chosen as potential glazes. This may appear unwarranted because of the high solubility in the pulverized form; however, their solubility as glazes in situ is much lower, as is shown by the values in table 5.

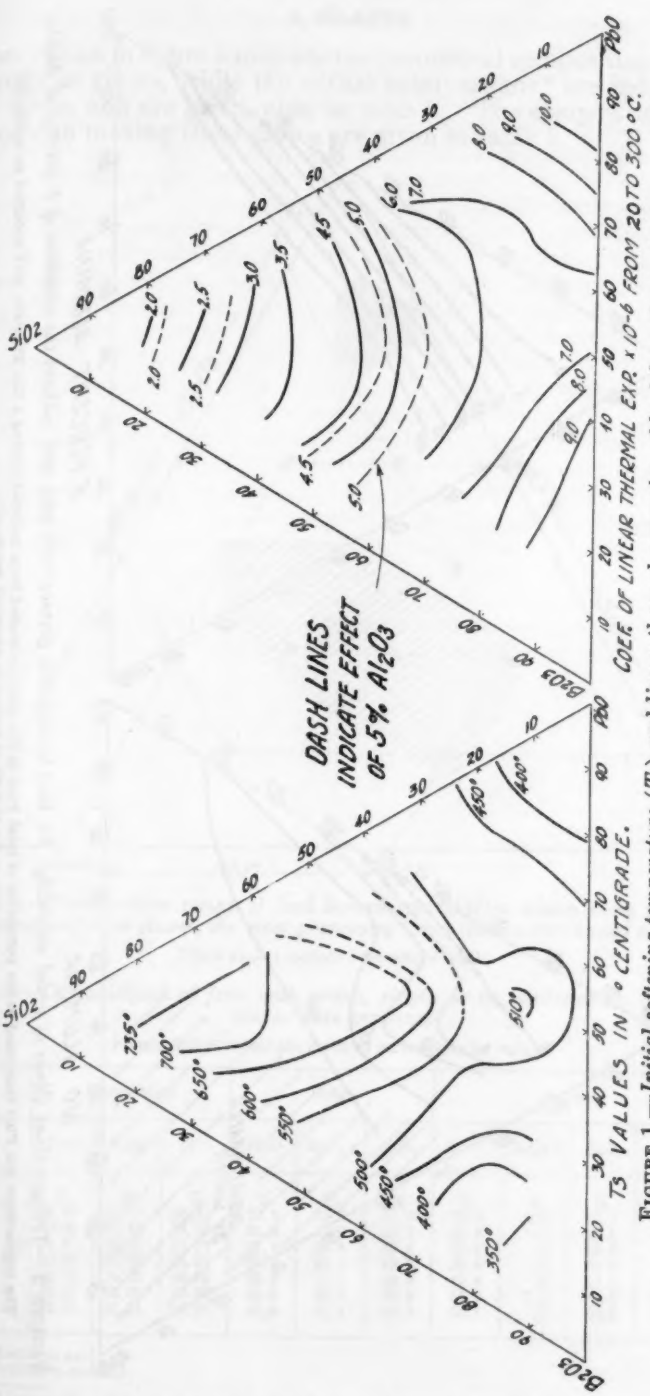
SiO2
B2O3
PbO
DASH LINES INDICATE EFFECT OF 5% Al2O3
COEF. OF LINEAR THERMAL EXP. x 10-6 FROM 20 TO 300 °C.
T3 VALUES IN ° CENTIGRADE.

FIGURE 1.—*Initial softening temperature (T_3) and linear thermal expansion of lead borosilicate glasses.*

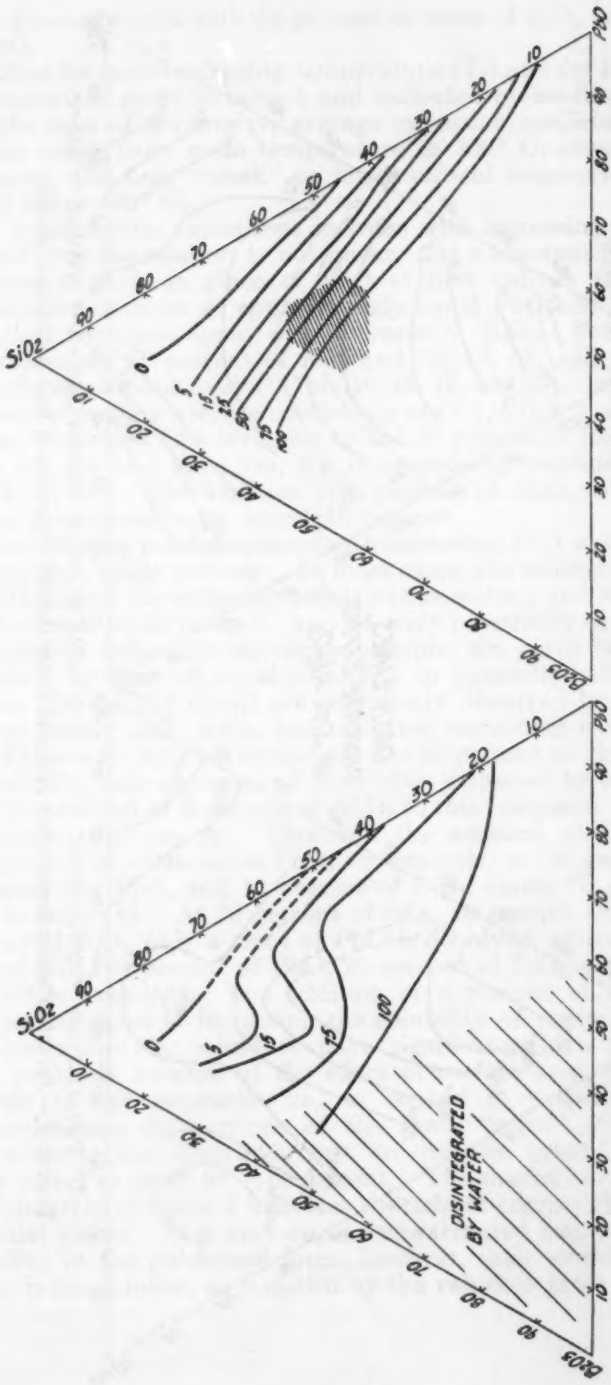

FIGURE 2.—*Isolytic lines (lines of equal solubility) for lead borosilicate glasses both with and without the addition of 5 percent of* Al_2O_3.

The values show the PbO (expressed as the percentage of total PbO in the glaze) extracted from material passing a No. 200 sieve, and retained on a No. 325 sieve, by ¼ hour of boiling in 4-percent acetic acid.

2. GLAZES

Open circles in figure 3 indicate the theoretical compositions selected for study as glazes, while the actual compositions [6] are indicated by filled circles and are given, also, in table 2. The compositions of the frits used in making these glazes are given in table 3.

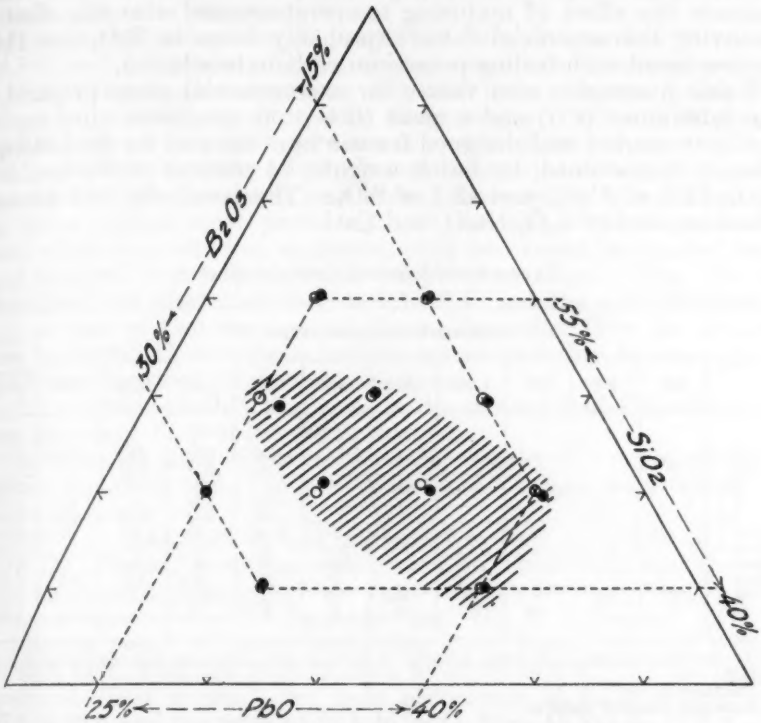

FIGURE 3.—*Composition range of lead borosilicate glasses which show promise of being useful as glazes, the most promising lying within the shaded area.*

These glasses contain 5 percent of Al_2O_3.

TABLE 3.—*Compositions of frits with which, singly or in combination, the various glazes were prepared*

[Composition values are given in percentages by weight]

Frit	Theoretical			Batch			Actual			
	PbO	B_2O_3	SiO_2	PbO	B_2O_3 [a]	SiO_2	PbO	R_2O_3 [b]	B_2O_3	SiO_2
	%	%	%	%	%	%	%	%	%	%
5	21.30	21.35	57.35	21.2	23.3	55.5	21.2	0.3	22.7	55.8
6	32.00	10.65	57.35	31.8	12.0	56.2	31.5	.4	11.8	56.3
8½	26.65	26.65	46.70	27.4	26.8	45.8	27.2	.8	25.5	46.5
8-13	26.65	32.00	41.35	27.1	33.3	39.6	26.5	.5	32.0	41.0
10	42.65	10.65	46.70	42.8	10.7	46.5	42.8	.5	10.2	46.5
13	32.00	32.00	36.00	31.9	32.6	35.5	31.1	1.1	30.0	37.8
14	42.65	21.35	36.00	42.6	21.9	35.5	42.1	.6	20.8	36.5

[a] Added as boric acid.
[b] Dissolved from crucible.

[6] Actual compositions differ from the theoretical because of PbO and B_2O_3 lost by volatilization during the fritting process.

Maturing ranges of the glazes were judged by the observations recorded in table 4. A glost temperature of 1,150° C (cone 4) was not exceeded because it was considered that satisfactory glazes of comparatively low thermal expansions and maturing at higher temperatures were already available. The "solubility" of the more promising glazes (shaded area, fig. 3) is given in table 5. The values indicate the effect of maturing temperature, and also the effect of removing the superficial "skin" (probably lower in B_2O_3 and PbO) by treatment with boiling potassium carbonate solution.

Table 5 contains also values for a commercial glaze prepared in the laboratory (*CB*) and a glaze (*Com.*) on specimens purchased in the open market and designed for use in ovens and for food storage. Glaze *CB* contained, by batch weights, 24 percent of PbO, 10.5 of B_2O_3, 13.5 of Al_2O_3, and 43.2 of SiO_2. The remainder (8.8 percent) was composed of K_2O, Na_2O, and CaO.

TABLE 4.—*Maturing ranges of glazes*[a]

Glaze	Maximum furnace temperature, °C										Best glost temperature
	925	950	975	1,000	1,025	1,050	1,075	1,100	1,125	1,150	
											°C
5-9							*SM*	*SM*	*SM*	*SM*	1,125
6-9								*SM*	*SM*	*M*	
8½					*SM*	*F*	*B*	*B*	*B*	*B*	1,125
9							*SM*	*SM*	*F*	[b]*F*	1,125
9½							*SM*	*SM*	*SM*	*SM*	1,125
8-13						*P*	*SM*	*F*	*F*	*B*	1,150
9-13					*M*	*SM*	*F*	*F*	*F*		1,100
9-14					*SM*	*SM*	*F*	*B*	*B*		1,100
10-14						*F*	*F*	*F*	[b]*B*	[b]*B*	1,100
13	*SM*	*SM*	*F*	*B*	*B*	[b]*B*					1,025
14	*F*	*B*	[c]*B*	[c]*B*	*B*	*B*	*B*				1,025

[a] Appearance is recorded as *B*, bright, or glossy; *F*, fair in general appearance; *SM*, semimatte; *M*, matte; *P*, poor.
[b] Tendency to run.
[c] Note high solubility (table 5).

TABLE 5.—*Solubility of glazes, estimated by comparing precipitated* PbS *suspension from solubility test with suspension of known* PbO *content and calculating to grams of* PbO *dissolved per 100 in.*[2] *of glaze surface*

Glaze	Glost temperature	PbO dissolved	Glaze	Glost temperature	PbO dissolved
	°C	g		°C	g
8½	1,050	0.0015	10-14	1,100	0.0018
8½	1,125	.0005	10-14	1,150	.0015
8½	1,125	[c].0025	14	975	.0240
8-13	1,075	.0008	14	1,000	.0100
8-13	1,150	.0005	14	1,025	.0015
9	1,125	.0005	14	1,025	[c].0400
9½	1,125	.0025	14	1,075	.0040
9-13	1,100	.0010	[b]*CB*	1,150	.0005
9-14	1,100	.0025	[c]*Com.*		.0005
			[c]*Com.*		[c].0005

[a] PbO dissolved in boiling 4-percent acetic acid, after having first treated glaze by boiling for 30 minutes in a 2 percent K_2CO_3 solution.
[b] A commercial "cone 3" glaze prepared and applied in the laboratory.
[c] Tests made on commercial "ovenware."

IV. DISCUSSION AND CONCLUSIONS

Although the laboratory work on this problem might have been prolonged by studying the effects of Al_2O_3 in percentages other than that reported on (5 percent), it is believed that the data obtained are sufficient to indicate the limited applicability of the lead borosilicate glasses as glazes.

Glasses containing over 55 percent of SiO_2, or less than 25 percent of PbO and 15 percent of B_2O_3, are too viscous to mature at or below 1,150° C (approximately "cone 4"), and those containing less than 40 percent of SiO_2, or more than 40 percent of PbO and 30 percent of B_2O_3, are too soluble regardless of maturing temperature. Of the compositions within the relatively small, six-sided area (figs. 2 and 3) not covered by the above limitations, those within the shaded area in figure 3 were most promising. Of the six compositions in this area which were studied as glazes, only two could be applied easily and matured over a fairly wide temperature range. One (No. 8½) appeared best after maturing at 1,125° C and the solubility was as low as that of two commercial glazes; the other (No. 14) matured best at 1,025° C, but the solubility would probably be too high for containers in which food might be stored.

The addition of Al_2O_3 to glasses in the ternary field PbO–B_2O_3–SiO_2 was necessary to prevent devitrification.

In terms of the "empirical formula" (molecular ratios with RO always equal to 1.0), the best glaze compositions were within the following limits:

PbO 1.0; Al_2O_3 0.28 to 0.43; B_2O_3 1.17 to 3.02; SiO_2 3.72 to 7.11.

W. M. Fickes,[7] working with glazes in which PbO was the only RO constituent, found that the ratio of SiO_2 to Al_2O_3 should be as 6:1, or higher. C. W. Parmalee and G. A. Williams,[8] after an exhaustive study of glazes containing B_2O_3, found 8⅓ mole percent of B_2O_3 best, with the ratio of SiO_2 to Al_2O_3 as 8:1. In the present group of "best glazes," the mole percentage of B_2O_3 ranged from 17.8 to 26.6 and the ratio of SiO_2 to Al_2O_3 from 12.8:1 to 17.2:1.

Considerable argument may be found in the earlier ceramic literature over the question of considering B_2O_3 as basic or as acid in the empirical formula, which in turn affects the calculation of the "oxygen ratio."[9] Preponderance of opinion appears to be in favor of considering B_2O_3 as basic.[10] It is interesting that, with the present data, if B_2O_3 be considered as basic, the oxygen ratios of the most promising glazes fall within the narrow range of 1.1 to 1.5 but, if considered as acid, they range from 6.4 to 10.2, and many glazes with ratios within this range are decidedly not usable. Binns (footnote 10) recommends an oxygen ratio of 2 for glazes containing boron, but Stull (footnote 10) found that a ratio 2 or higher produced opalescent glazes, while a ratio of 1.5 produced clear glazes.

The thermal expansion of each of the compositions studied as a glaze is significantly lower than that of typical commercial "semiporcelain" glazes. The average coefficient from room temperature to 300° C for the former ranges from approximately 3.7 to 4.4 $\times 10^{-6}$, and from approximately 5.5 to 5.8$\times 10^{-6}$ for the latter.

[7] Trans. Am. Ceram. Soc. **3**, 82 (1901).
[8] Trans. Am. Ceram. Soc. **18**, 812 (1916).
[9] An arbitrary ratio between the oxygen in the acid radicals and the oxygen in the basic radicals.
[10] C. F. Binns. Trans. Am. Ceram. Soc. **10**, 158 (1908). R. T. Stull. Trans. Am. Ceram. Soc. **12**, 129 (1910). F. G. Singer. Trans. Am. Ceram. Soc. **12**, 676 (1910).

Glazes 8½ and 14 were applied successfully on each of the talcose bodies described by Geller and Creamer (footnote 1) with the exception of bodies 1 to 4, inclusive, which contained no feldspar. Specimens which were glazed withstood an autoclave treatment in vapor at 400-lb/in.^{2} steam pressure for 4 hours without crazing and without perceptible loss of gloss. However, when immersed in the water, the gloss was affected.

The addition of Al_2O_3 increased resistance to solubility in some portions of the field, and decreased it in others.

The evaluation of laboratory data for relative solubility of lead-bearing glazes, for the purpose of establishing a maximum permissible without constituting a health hazard, is a complex problem. The following extract is from correspondence with W. B. White, of the Food and Drug Administration of the U. S. Department of Agriculture: "The writer's experience of some years on the contamination of foods with lead has left him somewhat skeptical of the value of any test other than actual trial of various types of foods under extreme conditions. This Administration has no official tolerances for Pb except in the case of fresh fruits, where, as yet, no less poisonous insecticides are available for pest control. Here the tolerance is 0.018 grain of Pb per pound of fruit, equivalent to 2.57 parts per million. This tolerance is a recognition that complete elimination by washing, though desirable, is impossible." W. P. Mason[11] states: "The writer believes that no water to be used for drinking purposes should contain lead compounds in quantity greater than what would correspond to half a part per million of metallic lead." Helpful information is contained in a report by G. W. Monier-Williams.[12] He found that 106 mg of lead per 100 in.^{2} of glaze surface, or 0.732 part per million parts of food under the conditions of his tests, were extracted by 1-percent citric acid, while cooking rhubarb extracted only 0.58 mg, or 0.004 part per million parts of food. Any laboratory test for solubility, involving the use of food or dilute acid as the solvent, might require a glazed vessel of standardized dimensions. For example, 100 in.^{2} of surface could be exposed conveniently to reaction in a vessel 4 in. in diameter and 8 in. deep by using approximately 1,400 g of dilute acid. Under such conditions the U. S. Food and Drug Administration's limit of 2.57 parts of lead (or 2.77 parts of PbO) per million of solvent would be equivalent to a maximum of 0.0039 g of PbO per 100 in.^{2} of exposed surface. Several of the glazes tested met this requirement, with 4-percent acetic acid as the solvent (table 5).

WASHINGTON, November 16, 1937.

[11] Examination of Water, J. Wiley & Sons, Inc., New York, N. Y.
[12] Report on Public Health and Medical Subjects No. 29 of the Ministry of Health; London, England.

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STRENGTH, WATER ABSORPTION, AND RESISTANCE TO FREEZING AND THAWING OF SAND-LIME BRICK

By John W. McBurney and Allan R. Eberle

ABSTRACT

The compressive and transverse strengths, water absorption, and penetrability of 120 specimens of sand-lime brick representing 11 plants were determined. Sieve analyses of sands from the same plants were also made. The same bricks were subjected to 50 cycles of freezing and thawing. It is concluded that resistance to freezing and thawing of sand-lime brick is estimated by strength when the bricks comply with the visual inspection clause of the American Society for Testing Materials' Specification for Sand-Lime Brick C 73–30.

CONTENTS

	Page
I. Introduction	67
II. Procedure and experimental data	68
1. Source and description of samples	68
2. Strength of bricks	68
3. Water absorption and penetrability	69
4. Sieve analysis of sands	70
5. Resistance to freezing and thawing	71
III. Discussion of data and conclusions	73
IV. Application of data to specification control of resistance to weathering	75
V. References	76

I. INTRODUCTION

Since the publication of the results of McMurdie's survey of the properties of sand-lime brick [1, 2] [1] the attention of investigators and specification writers has been increasingly directed to the question of durability of masonry units. As an illustration of this trend, the current tentative specification for clay building brick C 62–37T [3] abandons classifications based on strength and limits its grading to degrees of weather resistance. The investigation herein reported was undertaken therefore to determine the possibility of providing measures of the durability of sand-lime brick based upon correlation between physical properties and resistance to freezing and thawing.

[1] Figures in brackets here and elsewhere in the text refer to the references at the end of this paper.

Samples from 11 plants were selected in the present investigation (1936). Samples from 6 of these plants were selected by McMurdie [1] in 1928. The present paper, therefore, provides opportunity to compare the properties of bricks produced by these same six plants in 1928 and in 1936.

II. PROCEDURE AND EXPERIMENTAL DATA

1. SOURCE AND DESCRIPTION OF SAMPLES

Lots of 5 or 10 bricks each were selected from the 11 plants to give a representative range in quality of output from the principal brick-producing centers of the United States. Manufacturers *C*, *D*, *H*, and *K* submitted lots representing more than one sample. Table 1 gives data on the size, weight, and density of the bricks. Only average values are given since the individual specimens from any one sample differed from the mean of the sample by only 0.05 inch in any dimension; the weight of the individual specimens in no case varied from the mean by more than 0.5 pound; and there was no apparent correlation between weight and other properties.

TABLE 1.—*Average dimensions, weight, and density of sand-lime bricks*

Sample	Number of specimens [a]	Brick dimensions			Volume of brick	Weight per brick	Weight per cubic foot of brick	Density
		Length	Width	Depth				
		in.	in.	in.	in.^{3}	lb	lb	g/ml
A	10	8.00	3.75	2.26	67.9	4.28	108.8	1.74
B	10	8.50	3.94	2.40	80.1	5.12	110.5	1.77
C1	10	8.02	3.79	2.30	69.9	4.85	119.6	1.91
C2	5	8.02	3.79	2.30	69.9	4.98	123.1	1.97
D1	5	8.05	3.77	2.27	68.9	4.31	108.1	1.73
D2	5	8.05	3.78	2.31	70.3	4.44	109.1	1.75
E	10	8.02	3.75	2.26	68.0	4.25	108.0	1.73
F	10	8.29	3.76	2.24	70.0	4.36	107.6	1.72
G	10	8.05	3.75	2.34	70.5	4.78	117.2	1.88
H1	5	8.01	3.77	2.29	69.2	4.57	114.1	1.83
H2	5	8.00	3.75	2.27	68.5	4.60	116.0	1.86
I	10	8.02	3.75	2.29	68.8	4.42	111.0	1.78
J	10	8.02	3.75	2.32	69.9	5.20	128.5	2.06
K1	5	8.30	4.05	2.35	79.0	5.14	112.4	1.80
K2	5	8.30	4.05	2.37	79.7	5.51	119.5	1.91
K3	5	8.30	4.04	2.37	79.5	5.24	113.9	1.82
Average (120 specimens)		8.12	3.81	2.31	71.5	4.72	114.1	1.83

[a] The number of specimens applies also to tables 2 and 3.

2. STRENGTH OF BRICKS

Table 2 reports average values of the maximum and minimum strengths of the samples described in table 1. Where McMurdie reported tests from the same plants his data are given for comparison.

TABLE 2.—*Compressive strength (flatwise) and transverse strength of sand-lime brick*

Sample	Compressive strength, flatwise (lb/in.²)						Modulus of rupture (lb/in.²)						
	avg (*a*)	max	min	McMurdie			avg (*b*)	max	min	McMurdie			Ratio *b/a*
				avg	max	min				avg	max	min	
A	5,250	6,380	4,630	3,880	5,520	2,780	555	700	425	615	815	380	0.11
B	4,100	4,560	3,290				660	805	535				.16
C1	4,645	5,380	3,345	2,910	3,260	2,440	640	750	565	620	965	415	.14
C2	5,370	6,180	4,870				760	925	680				.14
D1	3,400	3,605	3,250				330	380	280				.10
D2	3,635	3,785	3,520				485	520	460				.135
E	5,135	5,960	4,300				735	865	630				.14
F	4,550	5,370	3,720	2,810	3,860	2,090	565	710	455	600	860	275	.12
G	4,180	4,730	3,250	3,930	5,140	2,680	540	605	500	690	995	295	.13
H1	4,705	5,105	4,075	3,770	5,010	2,620	530	575	490	550	670	455	.11
H2	4,785	5,110	4,420				515	580	400				.11
I	5,210	6,040	4,270				620	815	545				.12
J	7,615	8,360	6,730				975	1,125	870				.13
K1	3,620	4,320	3,260	2,310	3,730	1,260	825	925	710	460	765	180	.23
K2	3,800	5,590	2,840				797	945	692				.21
K3	3,235	3,500	2,950				640	755	285				.19
Average	4,754						643						
Average for comparison with McMurdie's tests	4,480			3,270			525			589			

The tests reported in table 2 were made according to the Standard Methods for Testing Brick [4] C 67–37 of the American Society for Testing Materials.

3. WATER ABSORPTION AND PENETRABILITY

Table 3 gives the percentage gain in weight after 24-hour cold immersion and after 5-hour boiling, and also the gain in weight (in grams) resulting from the partial immersion of whole brick flatwise in ⅛ inch of water for 3 minutes. Washburn [5] defined penetrability as "the ease with which a liquid is drawn into the pores of the body by capillary suction, without attendant chemical action between the body and the liquid," and described a method of test for penetrability which consisted in determining the gain in weight resulting from partial immersion of the test specimen in water for a predetermined time. The term "rate of absorption" does not properly apply to a gain in weight resulting from partial immersion for 3 minutes since, obviously, one point does not determine a rate. This paper, therefore, following Washburn, uses the term "penetrability" instead of "rate of absorption." Since the range in absorption by immersion in no case exceeded the mean ±1.8 percent, maximum and minimum absorption values are not given. McMurdie's results for penetrability are omitted, because they represent 5-minute partial immersion and hence are not directly comparable with the 3-minute tests.

TABLE 3.—*Water absorption and rate of absorption of sand-lime brick*

Sample	Water absorption test							
	24-hour cold immersion (average)		5-hour boiling (average)		Ratio	Penetrability during 3-min. of partial immersion in ¼ in. of water		
	C24	McMurdie	*B5*	McMurdie	*C24/B5*	Average	Maximum	Minimum
	%	%	%	%	g	g	g	g
A	13.7	13.4	18.4	18.1	0.74	29.0	49.0	21.0
B	12.9		18.2		.71	93.5	143.0	62.5
C1	10.4	14.0	14.7	18.8	.71	33.0	63.5	22.0
C2	10.0		13.9		.72	22.3	27.5	18.5
D1	13.0		18.7		.70	35.1	47.0	26.5
D2	13.5		18.8		.77	73.7	102.0	33.5
E	12.7		18.5		.69	49.8	85.0	24.0
F	11.8	15.9	16.4	21.6	.71	36.2	70.0	21.5
G	9.8	12.1	14.8	17.0	.66	60.4	86.5	46.5
H1	11.6	11.8	16.1	13.7	.72	31.7	37.5	27.5
H2	12.3		15.7		.78	29.9	33.5	27.0
I	13.1		17.8		.74	14.2	17.0	12.0
J	8.4		10.3		.81	12.9	15.0	9.5
K1	12.2	15.7	17.1	17.8	.72	105.4	140.0	77.5
K2	10.9		14.0		.78	36.1	47.0	21.0
K3	12.1		16.8		.72	71.6	87.5	60.0
Average	11.7		16.2		0.725	44.3		

Water absorption, like strength, was determined according to the American Society for Testing Materials Standard Methods for Testing Brick C 67–37.

4. SIEVE ANALYSES OF SANDS

Samples of sand were submitted by the same manufacturers that provided the bricks. Table 4 gives the results of sieve analyses of these sands. The wide range in grading is noteworthy. The percentage of sand by weight passing the No. 100 sieve ranged from 1 percent (sample *A*) to 51 percent (sample *I*). Sample *H* is discussed in connection with the freezing and thawing results.

TABLE 4.—*Sieve analyses of sands used in making sand-lime bricks*

Sample	Percentage of sand passing sieve No.—								
	3/8	4	8	16	30	40	50	80	100
	%	%	%	%	%	%	%	%	%
A	100	100	100	100	99	95	51	6	1
B	100	100	99	98	93	80	40	5	2
C	100	100	100	98	89	77	59	28	20
D	100	100	100	96	94	88	65	20	12
E	100	100	100	100	99	96	79	15	6
F	100	100	99	99	98	94	72	22	14
G	100	100	100	100	100	94	71	21	12
H	99	97	95	94	91	82	65	25	15
I	100	100	100	100	99	98	91	62	51
J	100	100	100	99	98	95	82	45	34
K	100	98	98	97	97	96	84	36	4

5. RESISTANCE TO FREEZING AND THAWING

Each specimen, as a half brick, was subjected to 50 cycles of freezing and thawing by the following method. The oven-dried bricks were weighed, totally immersed in water at room temperature for 4 hours and subjected to freezing for 20 hours standing on edge in ½ inch of water. Thawing was accomplished by total immersion in water at room temperature for 4 hours. After each fifth cycle of freezing and thawing, the bricks were stored in air for 44 hours, then totally immersed for 4 hours before starting another set of 5 cycles of freezing and thawing. After 25 cycles the specimens were oven-dried and weighed, and again oven-dried and weighed after 50 cycles.

This method differs from that used by McMurdie [2] principally in that McMurdie used a longer period of total immersion and permitted absorption to increase. From comparative tests on clay brick, it is concluded that McMurdie's method produces more rapid disintegration than the method described in this paper.

After completing 50 cycles of freezing and thawing, the compressive strength, flatwise, was determined on all the surviving bricks for comparison with the compressive strength on the other halves, which had been previously tested.

Table 5 summarizes the freezing and thawing data.

TABLE 5.—*Results of freezing and thawing of sand-lime bricks*

Sample	Number of specimens	Loss in weight after 25 cycles			Number of specimens rejected		Loss in weight after 50 cycles			Number of specimens rejected		Gain or loss in compressive strength		
		avg	max	min	3 percent loss	10 percent loss	avg	max	min	3 percent loss	10 percent loss	avg	max	min
		%	%	%			%	%	%			%	%	%
A	10	0.38	2.20	0.00	0	0	0.82	4.68	0.00	1	0	−11.0	+10.9	−21.6
B	10	.07	0.21	.00	0	0	.41	0.92	.09	0	0	−0.7	+8.0	−12.4
C1	10	.08	.37	.00	0	0	.26	.54	.05	0	0	+15.1	+21.9	−6.1
C2	5	.10	.14	.05	0	0	.10	.14	.05	0	0	+16.5	+36.2	+3.4
D1	5	1.90	3.65	.82	1	0	4.68	7.18	2.09	3	0	−18.7	−5.9	−38.6
D2	5	0.14	0.40	.05	0	0	0.45	1.31	0.10	0	0	−9.0	+2.7	−24.2
E	10	.10	.32	.00	0	0	.23	0.54	.00	0	0	−8.9	+0.6	−23.6
F	10	.12	.35	.00	0	0	.41	1.65	.00	0	0	−32.4	−15.6	−40.3
G	10	.14	.32	.00	0	0	.60	1.65	.14	0	0	0.0	+14.1	−9.0
H1	5	.63	.92	.30	0	0	2.14	3.31	.60	2	0	−11.6	−6.3	−17.6
H2	5	2.16	6.56	.29	1	0	[a] 8.0+	>10.0	2.12	4	3	[b] >−70.0	−13.3	−100.0
I	10	0.04	0.11	.00	0	0	0.28	0.53	0.11	0	0	−10.7	+9.6	−26.0
J	10	.05	.23	.00	0	0	.14	.21	.00	0	0	+20.9	+44.5	+11.7
K1	5	.68	2.82	.05	0	0	2.02	5.97	.23	1	0	0.0	+21.1	−12.4
K2	5	.17	0.33	.09	0	0	0.40	1.16	.00	0	0	+9.4	+44.0	−21.2
K3	5	.33	.53	.14	0	0	.58	1.10	.33	0	0	+0.9	+7.2	−6.4
All specimens	120		6.56	0.00	2	0		>10.0	0.00	11	3			

[a] Average includes 3 specimens with losses greater than 10 percent.
[b] Zero strength was ascribed to the 3 specimens that failed.

III. DISCUSSION OF DATA AND CONCLUSIONS

From the data presented in the preceding section the following conclusions appear justified:

1. The bricks produced by a given manufacturer are quite uniform in size. The American Society for Testing Materials' standard size for sand-lime brick [5] (2¼ by 3¾ by 8 inches with a permissible variation of ±1/16 inch in depth, ±⅛ inch in width, and ±¼ inch in length) is complied with, except for samples *B* and *K* in all dimensions and samples *G* and *J* in depth. Simplified Practice Recommendation R38–37 for sand-lime brick conforms to the American Society for Testing Materials' standard for size, except that the tolerance is ±⅛ inch instead of ±1/16 inch. This increased tolerance admits samples *G* and *J*.

2. The ratio of modulus of rupture to compressive strength ranges from 0.10 to 0.23; therefore, any prediction of one measure of strength from the other is subject to large error. The corresponding ratios on samples from the same plants previously tested by McMurdie are, in general, higher. The moduli of rupture are in fair agreement for the two series of tests, but the compressive strengths of the current series are notably higher.

3. McMurdie [1] reported for six plants an average compressive strength of 3,270 lb/in^2. Samples from the same six plants in 1936 averaged 4,480 lb/in^2. As the water absorption by 5-hour boiling was 17.8 percent for the 1928 samples and 15.9 percent for the 1936 samples, it is concluded that the gain in strength is actual and not due to differences in testing technique. Other things being equal, a decrease in water absorption is associated with an increase in strength. The two samples *A* and *H*, which show a marked increase in compressive strength without a corresponding decrease in water absorption, may have been subjected to increased time and temperature of steaming. It is reported that such a change in manufacturing method was made by several plants following the publication of McMurdie's results.

4. The ratio of water absorption cold to water abosrption by 5-hour boiling is unrelated to resistance to freezing and thawing of sand-lime bricks. This confirms the conclusion of McMurdie.

5. Contrary to the conclusions of McMurdie, there does not appear to be a consistent relation between the penetrability and resistance to freezing and thawing of sand-lime bricks.

6. Neither water absorption by cold immersion nor by 5-hour boiling is related to resistance to freezing and thawing according to the results of the present tests, thus confirming the results of McMurdie [2] for different makes of brick.

7. Confirming the conclusion previously reported by McMurdie, good correlation with resistance to freezing and thawing is given by the compressive strengths. Table 6 is a rearrangement of the data for the purpose of showing the relation between compressive strength and the results of 50 cycles of freezing and thawing.

TABLE 6.—*Results of 50 cycles of freezing and thawing, classified according to compressive strength (half-bricks flatwise) of specimens*

[Samples *H1* and *H2* omitted]

Range in compressive strength	Number of specimens	Average modulus of rupture	Original compressive strength	Average change in compressive strength after 50 cycles	Loss in weight after 50 cycles	
					Average	Maximum
Lb/in.²		Lb/in.²	Average lb/in.²	Percent	Percent	Percent
8,001 to 8,360	3	940	8,300	+20.5	0.15	0.18
7,501 to 8,000	3	990	7,720	+23.2	.11	.18
7,001 to 7,500	2	965	7,310	+26.7	.11	.14
6,501 to 7,000	2	1,015	6,735	+42.4	.20	.21
6,001 to 6,500	4	615	6,150	−11.6	.23	.40
5,501 to 6,000	8	690	5,690	−14.6	.29	1.11
5,001 to 5,500	16	680	5,310	−5.1	.27	1.14
4,501 to 5,000	20	620	4,740	−3.7	.24	0.62
4,001 to 4,500	18	615	4,310	−3.3	.45	1.65
3,501 to 4,000	17	590	3,740	−2.8	1.03	4.68
3,001 to 3,500	13	565	3,365	−3.0	2.33	7.18
2,840 to 3,000	4	585	2,930	+6.2	0.82	1.16

8. The results of the freezing and thawing tests are classified in table 7 according to modulus of rupture.

The correlation between modulus of rupture and change in compressive strength after 50 cycles of freezing and thawing is excellent. The relation between modulus of rupture and loss in weight after 50 cycles is somewhat more consistent than the relation of compressive strength to loss in weight given in table 6. Of the 10 specimens included in samples *H1* and *H2*, 8 fell in the grouping 501 to 600 lb/in.² for modulus of rupture and 2 in the grouping 401 to 500 lb/in.².

TABLE 7.—*Results of 50 cycles of freezing and thawing, classified according to modulus of rupture of specimens*

[Samples *H1* and *H2* omitted]

Range in modulus of rupture	Number of specimens	Average modulus of rupture	Original compressive strength 50 cycles	Average change in compressive strength after 50 cycles	Loss in weight after 50 cycles	
					Average	Maximum
Lb/in.²		Lb/in.²	Average lb/in.²	Percent	Percent	Percent
1,001 to 1,123	3	1,064	7,535	+31.2	0.13	0.21
901 to 1,000	8	952	6,425	+22.5	.24	1.23
801 to 900	11	839	5,310	+5.8	.42	2.98
701 to 800	18	734	4,500	−1.7	.64	5.97
601 to 700	27	644	4,745	+1.1	.29	1.14
501 to 600	28	547	3,735	−2.8	.45	1.65
401 to 500	8	461	3,815	−14.6	1.08	4.68
301 to 400	3	361	3,300	−15.9	4.80	7.18
281 to 300	4	288	3,895	−19.8	2.80	5.88

9. The sample of sand representing that used in manufacturing samples *H1* and *H2* contained clay balls retained on a ⅜-inch sieve. Five percent by weight of this sample failed to pass a No. 8 sieve. It is considered that the lack of resistance to freezing and thawing shown by samples *H1* and *H2* (see table 5) is explained by this peculiarity of the sand.

10. Freezing and thawing produced a marked increase in strength where the brick possessed high strength originally. McMurdie [2] also observed an increase in strength as did Kirkpatrick and Palmer [7] and Peppel [8].

11. Of the 120 specimens tested, 50 cycles of freezing and thawing would cause rejection of 11 specimens, if 3.0-percent loss of weight is taken as the criterion. The requirement of not exceeding 10-percent loss in weight would have rejected 3 specimens. The comparable samples tested by McMurdie gave a much higher incidence of failure. This is, in part, explained by the assumption that the method of freezing and thawing used in the present investigation is less severe, and in part, by the conclusion based upon strength and absorption data that the 1936 series of test specimens were of better quality.

On the basis of certain comparisons made with comparable samples of clay brick, it is considered that the method used in the present investigation corresponds in severity to that used by McBurney and Lovewell [9] in their investigation of the resistance to weathering of clay and shale brick.

IV. APPLICATION OF DATA TO SPECIFICATION CONTROL OF RESISTANCE TO WEATHERING

The Standard Specifications for Sand-Lime Building Brick C73–30 [5] classify sand-lime brick into three grades as shown in table 8.

TABLE 8

Grade	Compressive strength (bricks flatwise) mean gross area		Modulus of rupture (bricks flatwise) gross area	
	Mean of 5 tests	Individual minimum	Mean of 5 tests	Individual minimum
	lb/in.²	lb/in.²	lb/in.²	lb/in.²
A	4,500 or over	3,500	600 or over	400
B	2,500 to 4,500	2,000	450 or over	300
C	1,250 to 2,500	1,000	300 or over	200

A note is appended to this classification, which reads: "The above classifications are based on strength and do not necessarily measure weather resistance."

If the "individual minimum" in this classification is disregarded, the 120 bricks tested in this survey distribute, as shown in the third column of table 9, under the heading "Number of specimens."

The criterion "not more than 3.0-percent loss in weight or not more than 25.0-percent loss in strength" for passing 50 cycles of freezing and thawing is, in part, that used by McBurney and Lovewell[9] in their rating of clay and shale bricks. The justification for the more severe requirement "not more than 1.0-percent loss" is that the the majority of sand-lime brick show a progressive loss in weight with increasing number of cycles of freezing and thawing. For clay and shale brick, with the exception of certain soft-mud specimens, failure takes place suddenly and completely. The choice of 1-, 3-, 10-, or even 100-percent loss in weight as the criterion of failure after a given number of cycles would little affect the ratings of many clay and shale bricks. The purpose of the 1.0-percent loss in weight maximum for sand-lime brick is to insure that the rate of disintegration is negligible.

TABLE 9.—*Classification of results of 50 cycles of freezing and thawing according to American Society for Testing Materials grading (120 specimens)*

Grading of brick		Number of specimens	Not more than 3.0-percent loss in weight, or not more than 25.0-percent loss in compressive strength		Not more than 1.0-percent loss in weight, or not more than 25.0-percent loss in compressive strength	
Compressive strength	Modulus of rupture		Specimens passed	Specimens failed	Specimens passed	Specimens failed
			Number	*Number*	*Number*	*Number*
A	*A*	43	42	1	41	2
B	*A*	23	21	2	18	5
A	*B*	21	10	11	9	12
B	*B*	27	22	5	18	9
A	*C*	1	0	1	0	1
B	*C*	5	2	3	0	5

According to table 9, it appears that sand-lime bricks, grading *A* in both compressive strength and modulus of rupture, have a high probability of successfully withstanding 50 cycles of freezing and thawing by the method described in this paper. These data further indicate that a high transverse strength is more desirable than a high compressive strength for insuring resistance to frost action, if the two strengths are not in agreement. However, the poor showing of the *A* (compressive strength) *B* (modulus of rupture) combination is due to the fact that this classification included the *H1* and *H2* samples, which should be rejected under the "Inspection and Rejection" clause of the specification, which reads, in part, as follows:

"They shall be sound, of compact structure, reasonably uniform in shape and free from cracks, warpage, large pebbles, *balls of clay* [italics authors'] or particles of lime that would affect their serviceability or strength."

If this inspection and rejection clause can be made quantitative and enforceable, the *A*, *B*, and *C* grades of the sand-lime-brick specification C 73–30 could be regarded as equivalent in weather resistance to the *SW*, *MW*, and *NW* grades, respectively, of the Tentative Specifications for Building Brick (Made from Clay or Shale) C 62–37T [3] of the American Society for Testing Materials.

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APPROXIMATE GLASS CONTENT OF COMMERCIAL PORTLAND CEMENT CLINKER

By William Lerch [1]

ABSTRACT

The approximate glass content was determined, by the heat of solution method, for commercial portland cement clinker obtained from 21 plants throughout the United States. The approximate glass content of these commercial clinker compositions was found to vary from 2 to 21 percent. The approximate glass content was also determined for these clinker compositions after the clinker had been subjected to special heat treatment in the laboratory. The results indicate that for a given clinker composition, the heat of solution of the clinker, and likewise the glass content, are dependent on the cooling conditions to which the clinker has been subjected. Relatively high glass contents may be obtained by cooling the clinker rapidly, and relatively low glass contents by cooling it slowly.

CONTENTS

	Page
I. Introduction	77
II. Experimental procedure	78
1. Treatment of the clinker	78
2. Determination of the approximate glass content of the clinker	79
3. Estimation of the crystalline MgO in the clinker	80
III. Discussion	80
IV. References	81

I. INTRODUCTION

Numerous attempts to correlate the properties of commercial portland cements with their oxide composition or computed compound composition, have met with only partial success. Cements of almost identical composition, and ground to the same degree of fineness, have shown pronounced differences in physical properties.

These variations in properties are not due to differences in chemical composition but to some other cause, for instance the heat treatments to which the clinker has been subjected during or following clinkering.

At the clinkering temperatures attained by present-day methods of portland cement manufacture, a considerable part of the charge is present as a liquid phase, the percentage of liquid produced being dependent on the chemical composition of the charge and on the maximum temperature attained. The disposition of this liquid phase in the clinker will be dependent on the subsequent rate of cooling. If the cooling process is sufficiently rapid, a condition may be approached in which the liquid phase will be present as an "undercooled

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liquid" or glass. But if the cooling process is sufficiently slow to permit a continuous equilibrium, a completely crystalline product may be obtained. Intermediate rates of cooling may produce clinker of some degree of crystallization intermediate between these limits. The conditions of kiln operation which may be expected to affect the degree of crystallization, or conversely the glass content of the clinker are; the maximum kiln temperature; the rate at which the clinker passes through the kiln; the position of the hot zone with respect to the discharge end of the kiln; and the schedule of clinker cooling employed within the kiln and immediately subsequent to discharge from the kiln.

In a previous investigation by Lerch and Taylor [1] [2] it was found that the heat treatment of portland cement clinker has an important effect on some of the properties of the cement. The heat treatments employed in that study were of such character that different degrees of crystallization of the cement compounds and consequently different glass content might be anticipated, though the glass content was not determined quantitatively. A recent report by Lerch and Brownmiller [2] describes a heat of solution method for obtaining the approximate glass content of portland cement clinker. In the latter investigation it was found that rapidly cooled clinkers, prepared in an experimental kiln from commercial raw materials, contained relatively large quantities of glass.

The present report describes the results obtained for the approximate glass content, as determined by the heat of solution method, of 21 samples of standard portland cement clinker obtained from different plants throughout the United States as well as one additional sample of sulfate-resistant cement clinker. This report also contains the results obtained for the approximate glass content of these clinker compositions after they had been subjected to special heat treatments in the laboratory. The special heat treatments, to which the clinker was subjected in the laboratory, were of such character that different degrees of crystallization of the clinker compounds, consequently differences in the glass content, might be anticipated.

II. EXPERIMENTAL PROCEDURE

1. TREATMENT OF THE CLINKER

In the request to the plants which supplied the clinker, it was suggested that the clinker should be freshly burned, should not be water-quenched, and should not have been exposed to undue moisture on the stock pile. As a result of this request the samples, as received from the plants, were all of relatively low ignition loss.

Each clinker sample, as received, was crushed between rolls, thoroughly mixed, and divided into three lots, one lot to be used as received, one lot to be reburned and rapidly cooled, and one lot to be reburned and slowly cooled. These samples were prepared and reburned in laboratory kilns by W. C. Taylor following methods described in a previous report [1]. The clinker to be rapidly cooled was reburned in an experimental rotary kiln at 1,400° C. The clinker obtained from this kiln was small, not exceeding 0.5 inch in diameter, and in the operation of the kiln the clinker cooled from the clinkering tem-

[2] Numbers in brackets refer to literature references at the end of this paper.

perature to that of a dull-red heat, about 1,000° C, in 2 or 3 minutes. This clinker was designated "rapidly cooled clinker." The clinker to be slowly cooled was placed in an updraft gas-fired kiln and heated to 1,400° C. The gas and air were then adjusted in such manner as to allow the temperature of the clinker to decrease slowly over a 2-hour period to 1,250° C. The gas and air were then cut off and the clinker was allowed to cool with the kiln. This clinker was designated "slowly cooled clinker." The third lot of clinker was used as received from the plant and was designated "plant clinker."

2. DETERMINATION OF THE APPROXIMATE GLASS CONTENT OF THE CLINKER

The determination of the approximate glass content of portland cement clinker, by the heat of solution method, is dependent on the latent heat of crystallization of the liquid phase. Thus it becomes necessary to prepare a crystalline material of each clinker sample. The crystallized materials were prepared by carefully "annealing" [3] a small quantity of the plant clinker in an electric furnace. The samples were placed in the furnace and heated to 1,400°C. The temperature of the furnace was caused to drop slowly over a period of 2 hours to 1,250° C, which is slightly below the temperature of final solidification of the liquid, and the charge was held at that temperature ±10° C for 15 hours.

The heats of solution were determined, by the use of a vacuum-flask calorimeter [3], for the rapidly cooled clinker, the slowly cooled clinker, the plant clinker and the crystalline material obtained by "annealing" in the electric furnace. The heats of solution were determined in duplicate and the duplicate determinations agreed to within 3 cal/g in every case.

Table 1 gives the complete data for all of the clinker samples used in this investigation, including the partial oxide composition, the calculated compound composition as computed by Bogue [4] and Dahl [5], the Al_2O_3/Fe_2O_3 ratio, the heats of solution on the ignited weight basis, and the approximate glass content of the clinker.

The clinker compositions which were "annealed" in the electric furnace and those which were slowly cooled in the updraft gas-fired kiln showed various degrees of dusting. Complete dusting occurred with some samples when "annealed" in the electric furnace and partial dusting occurred in some of the slowly cooled samples. There was no evidence of dusting with any of the plant clinker or any of the clinker which was rapidly cooled.

Since dusting, which is the result of beta to gamma inversion of $2CaO.SiO_2$, involves a thermal change, it was necessary to make a correction for this thermal change before calculating the approximate glass content of the clinker. Johannson and Thorvaldson [6] found that the heat involved in the transition of $2CaO.SiO_2$ from the beta to gamma modification was 6.0 cal/g at 20° C. Thus for the compositions which dusted completely, when annealed in the electric furnace, a correction of 0.06 cal/g for each 1 percent of $2CaO.SiO_2$ was added to the obtained heats of solution. For the annealed compositions which

[3] The term "annealing", as used in this report, involves a slow cooling process which might be expected to produce a maximum degree of crystallization.

showed only slight dusting or no dusting, no corrections were applied to the obtained heats of solution.

The difference between the heat of solution of a given lot of clinker and the corrected heat of solution of the same clinker "annealed" in the electric furnace constitutes the basis for calculating the approximate glass content for the clinker [2]. It is shown in table 1 that these differences are always positive for the plant clinker and for the rapidly cooled clinker, but that they are sometimes negative for the slowly cooled clinker. These negative values obtained with the slowly cooled clinker may be accounted for as a result of small errors in the determination of the heats of solution, and as a result of thermal changes involved in the partial inversion of beta to gamma $2CaO.SiO_2$ in some of the slowly cooled samples.

3. ESTIMATION OF THE CRYSTALLINE MgO IN THE CLINKER

In making the determinations of heats of solution it was found that periclase, crystalline MgO, as present in the clinker dissolved slowly in the acid solution. This suggested the possibility of a separation of MgO by the solution method. The sample of ground clinker was introduced into the calorimeter in the usual manner and the stirring continued for 10 minutes. The solution was then filtered on a suction filter and the residue ignited and weighed. By microscopic examination it was observed that these insoluble residues consisted almost entirely of periclase, with not more than a trace of other material present. It was found that for a clinker of low MgO content, less than 2.0 percent, this insoluble residue would be very low regardless of the cooling conditions to which the clinker had been subjected. With a clinker of higher MgO content, 2.4 percent or more, a larger insoluble residue was obtained by this method, and the quantity of insoluble residue varied with each clinker composition, depending on the method of cooling the clinker. A larger insoluble residue was obtained from the slowly cooled clinker than that obtained from the rapidly cooled clinker of the same composition. This seems to give further evidence that in the rapidly cooled clinker part of the MgO was dissolved in the glass with the result that this clinker contained less crystalline MgO, periclase, than did the corresponding slowly cooled clinker. The results of these determinations of insoluble MgO are given in table 1. It should be borne in mind that these results do not represent the quantity of periclase present in the clinker, since part of the periclase has dissolved during the 10-minute stirring interval.

III. DISCUSSION

The clinker samples used in this investigation were obtained from 21 plants throughout the United States; the range of their oxide composition represents the approximate range of the clinker compositions used in the manufacture of standard portland cement at the present time. It also seems probable that the methods of manufacture employed at these various plants constitute a representative cross section of present-day manufacturing processes.

The approximate glass content of the plant clinker was determined by the heat of solution method. The approximate glass content was also determined for these clinker compositions after they had been

TABLE 1.—*Analysis, calculated composition, and approximate glass content of com*

Clinker [1]	Chemical composition [2]									Major constituents, correct			
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Loss on ignition	Insoluble residue	Free CaO	SiO_2	Fe_2O_3 less FeO as Fe_2O_3	Al_2O_3 less TiO_2	CaO, less free CaO
	%	%	%	%	%	%	%	%	%	%	%	%	%
1S 13721									0.4				
1P 13722	21.5	2.2	6.3	64.3	3.0	0.7	0.4	0.2	1.2	21.5	2.2	6.0	63.1
1Q 13723									1.5				
2S 13724									0.1				
2P 13725	20.6	5.7	6.0	64.1	1.8	.6	.2	.2	.8	20.6	5.5	5.6	63.3
2Q 13726									.9				
3S 13727									.2				
3P 13728	22.4	2.7	5.9	63.9	4.0	.1	.3	.2	.4	22.4	2.3	5.4	63.5
3Q 13729									.4				
4S 13730									.3				
4P 13731	19.8	7.0	5.1	62.7	4.2	.1	.2	.4	4.2	19.8	5.3	4.7	58.5
4Q 13732									1.6				
6S 13736									0				
6P 13737	21.7	3.1	6.2	66.6	1.4	.3	.2	.2	.4	21.7	3.1	5.9	66.2
6Q 13738									.5				
7S 13739									tr				
7P 13740	21.1	2.4	7.2	64.2	3.4	.4	.2	.2	.4	21.1	2.4	6.9	63.8
7Q 13741									.6				
8S 13742									.1				
8P 13743	22.5	3.0	5.3	64.5	3.5	.3	.3	.1	.6	22.5	3.0	4.9	63.9
8Q 13744									.8				
9S 13745									.1				
9P 13746	22.7	2.2	5.9	63.6	4.2	.3	.3	.3	.8	22.7	2.2	5.6	62.8
9Q 13747									.9				
10S 13748									.2				
10P 13749	23.5	2.9	5.1	65.0	1.3	.6	.5	.2	2.1	23.5	2.9	4.8	62.9
10Q 13750									2.0				
11S 13751									0.1				
11P 13752	22.0	5.1	4.9	66.3	0.8	.1	.2	.2	.2	22.0	5.1	4.6	66.1
11Q 13753									.3				
12S 13754									0				
12P 13755	22.0	6.2	5.2	63.1	2.4	.2	.3	.3	tr	22.0	6.2	4.9	63.1
12Q 13756									.1				
13S 13757									.1				
13P 13758	21.9	2.7	5.8	64.1	4.3	.4	.2	.2	.4	21.9	2.7	5.4	63.7
13Q 13759									.6				
14S 13760									tr				
14P 13761	21.9	2.5	5.3	64.2	3.9	.5	.4	.3	.9	21.9	2.5	5.0	63.3
14Q 13762									.8				
15S 13763									.1				
15P 13764	21.8	3.0	5.7	63.4	4.2	.6	.3	.1	1.3	21.8	3.0	5.4	62.1
15Q 13765									1.4				
16S 13766									0				
16P 13767	22.3	2.6	6.3	65.0	3.3	.2	.2	.2	.4	22.3	2.2	6.0	64.6
16Q 13768									.3				
17S 13769									.2				
17P 13700	23.0	2.6	6.2	66.9	1.3	tr	.2	.2	.4	23.0	2.6	5.8	66.5
17Q 13771									.5				
18S 13772									.1				
18P 13773	21.7	2.7	6.1	64.4	3.6	0.3	.2	.1	.8	21.7	2.1	5.8	63.6
18Q 13774									.5				
19S 13775									tr				
19P 13776	22.1	2.8	5.5	63.4	4.7	.3	.2	.1	.6	22.1	2.8	5.2	62.8
19Q 13777									.5				
20S 13778									.3				
20P 13779	19.9	3.9	7.5	66.0	1.0	.6	.4	.2	1.3	19.9	3.9	7.0	64.7
20Q 13780									1.4				
21S 13781									.1				
21P 13782	20.9	3.0	7.6	66.0	1.3	.3	.4	.2	.4	20.9	3.0	7.2	65.6
21Q 13783									.4				
22S 13784									0				
22P 13785	21.9	2.6	6.0	63.4	4.4	.2	.2	.2	.3	21.9	2.6	5.7	63.1
22Q 13786									.2				
23S 13787									.9				
23P 13788	19.9	2.5	7.4	65.4	3.1	.4	.3	.2	2.0	19.9	2.4	7.0	63.4
23Q 13789									1.6				

[1] S, slowly cooled clinker; P, plant clinker; Q, rapidly cooled clinker.
[2] Chemical analysis by C. L. Ford.
[3] The estimated uncertainty of these heat-of-solution values was ±2.0 cal/g.
[4] Stirring for 10 min in 420 g of 2*N* HNO_3 containing 10 ml of 48 percent of HF.

Washington, November 17, 1937.

tent of commercial portland cement clinker and the glass contents of the same clinker after b

tuents, corrected			Additional minor constituents				Calculated compound composition						
Al_2O_3 less TiO_2	CaO, less free CaO	MgO	FeO	TiO_2	Na_2O	K_2O	C_3S	C_2S	C_3A	C_4AF	MgO	Free CaO	Al_2O_3/Fe_2O_3
%	%	%	%	%	%	%	%	%	%	%	%	%	
6.0	63.1	3.0	0	0.3	0.1	1.6	50.0	24.0	12.2	6.7	3.0	1.2	2.9
5.6	63.3	1.8	.2	.4	.3	0.7	55.5	17.2	5.6	16.7	1.8	0.8	1.1
5.4	63.5	4.0	.4	.5	.6	.2	48.5	27.7	10.4	7.0	4.0	.4	2.2
4.7	58.5	4.2	1.5	.4	.5	.2	48.3	20.3	3.5	16.1	4.2	4.2	0.8
5.9	66.2	1.4	0	.3	.1	.1	60.5	16.7	10.4	9.4	1.4	0.4	2.0
6.9	63.8	3.4	tr	.3	.4	.6	49.6	23.1	14.2	7.3	3.4	.4	3.0
4.9	63.9	3.5	0	.4	.2	.5	51.9	25.4	8.0	9.1	3.5	.6	1.8
5.6	62.8	4.2	0	.3	.4	.5	42.3	33.1	11.1	6.7	4.2	.8	2.7
4.8	62.9	1.3	0	.3	.3	.8	41.0	36.5	7.8	8.8	1.3	2.1	1.8
4.6	66.1	0.8	0	.3	.7	.2	63.7	15.0	3.6	15.5	0.8	0.2	1.0
4.9	63.1	2.4	tr	.3	.3	.4	47.9	27.0	2.5	18.9	2.4	tr	0.8
5.4	63.7	4.3	0	.4	.2	.6	52.7	23.1	9.8	8.2	4.3	0.4	2.1
5.0	63.3	3.9	0	.3	.3	1.0	54.0	22.0	9.1	7.6	3.9	.9	2.1
5.4	62.1	4.2	0	.3	.3	0.9	46.6	27.4	9.2	9.1	4.2	1.3	1.9
6.0	64.6	3.3	.4	.3	.2	.4	50.0	26.3	12.2	6.7	3.3	0.4	2.4
5.8	66.3	1.3	0	.4	.1	.2	53.3	25.7	11.0	7.9	1.3	.4	2.4
5.8	63.6	3.6	.5	.4	.2	.8	52.0	23.0	11.8	6.4	3.6	.8	2.3
5.2	62.8	4.7	0	.3	.3	.8	48.8	26.6	9.1	8.5	4.7	.6	1.9
7.0	64.7	1.0	0	.5	.2	.8	59.5	12.2	12.0	11.9	1.0	1.3	1.9
7.2	65.6	1.3	0	.4	.4	.6	55.6	18.0	14.0	9.1	1.3	0.4	2.5
5.7	63.1	4.4	0	.3	.5	.9	48.3	26.3	10.7	7.9	4.4	.3	2.3
7.0	63.4	3.1	.1	.4	.5	.5	55.1	14.6	14.6	7.3	3.1	2.0	3.0

r after being subjected to special heat treatments

	Al_2O_3/Fe_2O_3	Heat of solution—ignited basis [3]				Approximate glass content	MgO remaining insoluble at 10 min [4]	Clinker [5]
		Annealed in electric furnace		Kiln product (obtained)	Difference			
		Obtained	Corrected for C_3S inversion					
		cal/g	*cal/g*	*cal/g*	*cal/g*	%	%	
				642.6	−1.2	0	0.8	1S
.2	2.9	642.3	643.8	644.8	+1.0	2	.2	1P
				648.0	4.2	8	.2	1Q
				629.1	0.6	1	.1	2S
.8	1.1	627.3	628.5	630.6	2.1	5	.1	2P
				637.4	8.9	21	.1	2Q
				638.5	−0.6	0	1.1	3S
.4	2.2	637.3	639.1	644.4	+5.3	11	0.6	3P
				647.2	8.1	16	0.5	3Q
				633.2	0.6	1	1.3	4S
.2	0.8	632.6	632.6	641.1	8.5	21	0.6	4P
				641.7	9.6	22	.5	4Q
				640.3	1.6	3	.1	6S
.4	2.0	638.7	638.7	639.5	0.8	2	.1	6P
				645.5	6.8	14	.1	6Q
				645.9	0.8	2	.8	7S
.4	3.0	645.1	645.1	649.3	4.2	8	.4	7P
				655.5	10.4	21	.2	7Q
				637.8	−0.6	0	.7	8S
.6	1.8	636.8	638.4	643.5	+5.1	11	.4	8P
				644.2	5.8	12	.4	8Q
				637.4	0.1	0	1.0	9S
.8	2.7	635.2	637.3	641.5	4.2	8	0.4	9P
				644.1	6.8	14	.3	9Q
				623.8	0.5	1	.1	10S
.1	1.8	621.0	623.3	624.1	.8	2	.1	10P
				628.2	4.9	10	.1	10Q
				630.5	1.1	3	.1	11S
.2	1.0	629.4	629.4	632.3	2.9	7	.1	11P
				632.7	3.3	8	.1	11Q
				619.5	0.4	1	.6	12S
tr	0.8	619.1	619.1	623.1	4.0	9	.2	12P
				627.7	8.6	21	.2	12Q
				646.8	−1.2	0	1.2	13S
.4	2.1	648.0	648.0	649.8	+1.8	4	0.7	13P
				655.2	7.2	15	.5	13Q
				646.5	−0.7	0	1.0	14S
.9	2.1	645.8	647.2	650.4	+2.8	6	0.5	14P
				654.7	7.5	15	.4	14Q
				636.7	1.0	2	1.3	15S
.3	1.9	635.7	635.7	638.0	2.3	5	0.6	15P
				643.7	8.0	16	.5	15Q
				643.0	−1.2	0	.5	16S
.4	2.4	642.5	644.2	649.9	+5.7	11	.2	16P
				652.8	8.6	17	.1	16Q
				637.0	−0.2	0	.1	17S
.4	2.4	635.5	637.2	639.5	+2.3	5	.1	17P
				643.2	6.0	12	.1	17Q
				640.2	−0.6	0	.9	18S
.8	2.3	639.3	640.8	645.8	+5.0	10	.3	18P
				649.7	8.9	18	.3	18Q
				641.1	0.2	0	.8	19S
.6	1.9	639.2	640.9	644.2	3.3	7	.3	19P
				646.3	5.4	11	.3	19Q
				639.0	1.2	2	.1	20S
.3	1.9	637.8	637.8	639.0	1.2	2	.1	20P
				644.0	6.2	13	.1	20Q
				646.8	0.7	1	.1	21S
.4	2.5	646.1	646.1	648.5	2.4	5	.1	21P
				650.6	4.5	9	.1	21Q
				641.6	−2.7	0	1.1	22S
.8	2.3	642.6	644.3	645.6	+1.3	3	0.8	22P
				649.9	5.6	11	.5	22Q
				656.6	0.9	2	.8	23S
.0	3.0	655.7	655.7	658.3	2.6	5	.3	23P
				661.3	5.6	11	.2	23Q

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subjected to special heat treatments in the laboratory. The special heat treatments, to which the clinker was subjected in the laboratory, were of such character that different degrees of crystallization of the clinker compounds, and consequently different glass contents might be anticipated.

Factors other than glass content which may cause some slight variations in the heat of solution of the clinker have been discussed in a previous paper [2].

The results obtained from this investigation indicate that, for a clinker of given oxide composition, the heat of solution of the clinker, and likewise the glass content, will be dependent on the cooling conditions to which the clinker has been subjected. The largest heat of solution of a given clinker, that is the highest glass content, was obtained from the rapidly cooled clinker. The slowly cooled clinker always gave a lower heat of solution and was, therefore, of low glass content. In some instances the glass content of the plant clinker as received was of the same order as the minimum glass content of the slowly cooled laboratory clinker. In other cases the glass content of the plant clinker closely approached the maximum glass content obtained in the rapidly cooled laboratory clinker. This seems to indicate that the cooling rates attained in commercial practice vary in sufficient degree to produce large differences in the glass content of commercial clinker.

In a previous investigation [1] it was found that the heat treatment of portland cement clinker has an important effect on some of the properties of the cement. The heat treatments used in that investigation were essentially the same as the special laboratory heat treatments which were used in this investigation and which have now been shown to produce different glass contents in the clinker. Since the commercial products used in this investigation have been found to vary greatly in glass content, it seems probable that the variations in properties of commercial cements, which cannot be accounted for on the basis of composition, may be partly or entirely accounted for from a consideration of their glass content.

Previous investigators [2, 7, 8] have found that a considerable quantity of MgO dissolves in the liquid formed at the clinkering temperatures, and when the compositions were cooled rapidly this MgO remained in solution in the glass. The qualitative results of insoluble MgO, as obtained in this study, give further evidence of the solution of MgO in the glass. For each composition containing 2.4 percent of MgO, or more, the largest percentages of insoluble MgO were obtained from the slowly cooled clinker, whereas the lowest percentages were obtained from the rapidly cooled clinker.

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Washington, November 17, 1937.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1067

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A LABORATORY EXTRACTION APPARATUS AND ITS USE IN SEPARATING A LUBRICATING-OIL FRACTION WITH ACETIC ACID [1]

By Sylvester T. Schicktanz [2]

ABSTRACT

There is described a glass laboratory extraction apparatus, operating with reflux, for use with solvents heavier than the liquids to be extracted. Data are given on the extraction, with acetic acid, of a narrow-boiling fraction of "water-white" lubricating oil.

CONTENTS

	Page
I. Introduction	83
II. Apparatus and experimental procedure	85
III. Results	85

I. INTRODUCTION

Solvent extraction is often useful for the separation of complex liquid mixtures when other methods of fractionation are not effective. Saal and van Dyck [3] pointed out the similarity between solvent extraction and distillation, the solvent phase in extraction being analogous to the vapor phase in distillation, and emphasized the importance of the reflux ratio in extraction. Similar calculations on the theory of solvent extraction with reflux were made by Fenske and his coworkers,[4,5,6] who applied the principles in actual practice and effectively separated narrow-boiling cuts of lubricating oils by this method.

The present paper describes a glass laboratory extracting column, operating with reflux, for use with solvents denser than the liquid being extracted. This is a modification of the larger columns developed by Fenske and his coworkers.[7] Data are also given on the use of this column in extracting a narrow-boiling fraction of "water-white" lubricating oil with acetic acid.[8]

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

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[6] M. R. Fenske and W. B. McCluer. U. S. Patents 2037318 and 2037319
[7] See footnote 5.
[8] For the description of a 14-m column for use with solvents less dense than the material to be extracted, see B. J. Mair and S. T. Schicktanz, J. Research NBS **17**, 909 (1936) RP953.

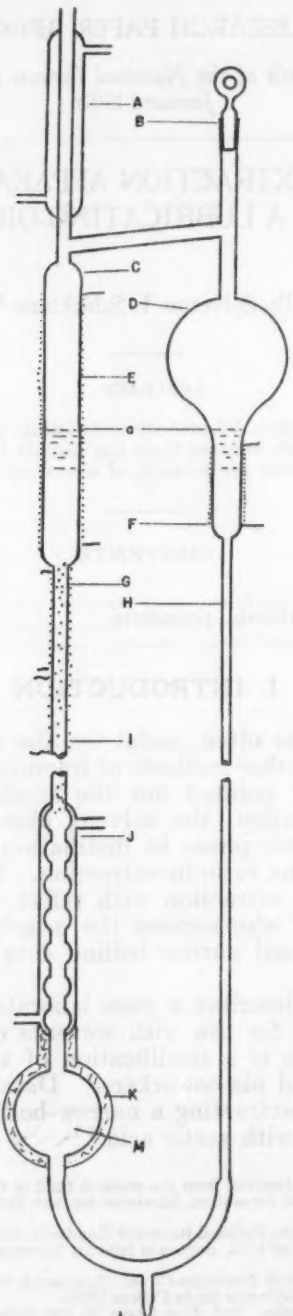

FIGURE 1.—*Diagram of glass extraction apparatus for use with solvents heavier than the liquid to be extracted.*

[The description is given in the text.]

II. APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus is shown schematically in figure 1. The solvent is first placed in the apparatus to the height, *a*. The material to be extracted is then introduced through the condenser, *A*, into the section *C*, where it floats on the surface of the solvent. By means of the heater, *F*, the solvent in the evaporator, *D*, is distilled over into section *C*, the vapor being liquefied in the condenser, *A*. The evaporator, *D*, is an inverted 500-ml Kjeldahl flask, the lower section of which has fine particles of carborundum fused on the inner surface to insure uniform boiling. *B* is a ground joint. Section *C* is warmed by means of the heater, *E*, in order to increase the solubility of the material being extracted as the solvent passes down through it. For some distance below the section *C*, the temperature gradient of the tube, *G*, which has an outside diameter of about 8 mm, is controlled by means of the electrical heating unit, *I*. The saturated solution, gradually cooling, passes down the tube, *G*, to the cooled section, *J*, where most of the dissolved material is precipitated and returns up the tube in the form of small globules. The 200-ml flask, *M*, below the section *J*, serves to allow the finer particles, formed in *J* and carried down by the flow of the solution, to coalesce, because of the decreased velocity of flow, and rise up the tube, *G*, rather than be carried across to the tube, *H*, which returns the solution to the evaporator, *D*, to be recirculated. The flask, *M*, is covered with a 0.5-in. layer of magnesia, *K*. By means of a suction tube inserted through the opening at *B*, there is withdrawn from the evaporator, *D*, at appropriate intervals, such an amount of solution as will contain the quantity of material desired for one fraction. An amount of solvent equivalent to that in the solution withdrawn at *D* is added to the system through the condenser, *A*. The column is drained by breaking the lower tip, *L*. The tubes, *G* and *H*, are made as long as practicable, as the effectiveness of separation depends to a great extent on the length of column. The optimum dimensions of the tubes, *G* and *H*; the boiler, *D*; the sections *C* and *J*; and the flask, *M*, are a function of the quantity of material being extracted and of the solubility of the various constituents in the solvent. The rate of evaporation of solvent from the boiler, *D*, which determines the rate of circulation of solvent through the system (counterclockwise, as sketched), is adjusted to a value below that at which the circulation will be so rapid as to carry globules of oil across the lower end of the apparatus from the flask, *M*, to the tube, *H*.

III. RESULTS

In table 1 are given the physical properties of the original fraction of "water-white" lubricating oil [9] and of the fractions obtained by solvent extraction with reflux in a column 14 m long, using acetic acid as the solvent. In this experiment, the temperature of the cooling section, *J*, was kept at about 17° C, in order to avoid solidification of acetic acid and to obtain the maximum separation possible. Fractions were withdrawn at intervals of about 12 hr.

[9] For a description of the "water-white" oil and its constituents, see B. J. Mair and S. T. Schicktanz, J. Research NBS **17**, 909 (1936) RP953; B. J. Mair and C. B. Willingham, J. Research NBS **17**, 943 (1936) RP954.

TABLE 1.—*Physical properties of lubricating-oil fractions obtained by solvent extraction with acetic acid in a 14-m column*

Number of fraction	Weight percentage of charge	Refractive index n_D^{25}	Kinematic viscosity at		Kinematic-viscosity index [1]	Boiling point at 1-mm Hg pressure
			100° F	210° F		
	%		*Stoke*	*Stoke*		°C
Original		1.4703	0.2563	0.0447	102	
1	9.41	1.4839	.3931	.0539	70	190
2	6.74	1.4811	.3517	.0511	76	
3	11.82	1.4775	.3288	.0497	82	
4	14.40	1.4775	.3126	.0485	89	
5	7.18	1.4721	.2834	.0466	94	
6	9.67	1.4687	.2557	.0442	99	
7	9.12	1.4663	.2333	.0431	113	
8	5.75	1.4640				
9	11.37	1.4617	.1999	.0399	124	
10	7.17	1.4590	.1833	.0385	134	
Residue	7.06	1.4563	.1734	.0378	141	207

[1] These viscosity indices were computed with the aid of the tables of R. E. Hersh, E. K. Fisher, and M. R. Fenske, Ind. Eng. Chem. **27**, 1441–46 (1935).

The extent of the separation obtained by this method is clearly shown by a comparison of the physical properties of the fractions with those of the original oil. Coloration of the oil occurred during the extraction with acetic acid, the greater part of the color being concentrated in the first fractions. This coloration did not appear to affect very much the physical properties of the oil, as the recombination of the separated fractions gave a composite whose physical properties, except for the dark color, were nearly identical with those of the original oil.[10]

WASHINGTON, November 17, 1937.

[10] Note added in proof: Since this report was prepared, the author has noted a publication on an *Apparatus for the extraction of solutions with heavy solvents*, by S. Wehrli, Helv. Chim. Acta. **20**, 927 (1937).

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RESEARCH PAPER RP1068

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VOLUMETRIC DETERMINATION OF ALPHA-, BETA-, AND GAMMA-CELLULOSE IN PULPS AND IN PAPERS CONTAINING SIZING, FILLER, AND OTHER MATERIALS

By Herbert F. Launer

ABSTRACT

The volumetric method for the determination of alpha-, beta-, and gamma-cellulose, previously described in Bureau Research Paper RP979 is shown to be applicable to papers containing rosin, glue, starch, oxidizable fillers and lignin, and to pulps containing natural resins in any amount. As the method depends upon the estimation of each cellulose fraction by oxidation with dichromate, and as the sizing materials are all oxidizable, the manner of making corrections for these materials is described in detail. The alpha-cellulose values so obtained are shown to be in good agreement with those of a gravimetric method for a wide range of pulps and papers. The relative shortness of the volumetric procedure is especially apparent when the papers contain mineral fillers or lignin, as these are removed when necessary rather than estimated and corrected for.

CONTENTS

	Page
I. Introduction	87
II. Analytical procedure	88
III. Comparison of the volumetric and gravimetric results for alpha-cellulose	89
IV. Corrections for the sizing materials	90
1. Dichromate equivalents of the sizing materials	90
2. Distribution of the sizing materials among the three cellulose fractions and the method of applying the corrections	91
(a) Alpha fraction	91
(b) Gamma fraction	92
V. Dichromate equivalents for cellulose and lignin	93
VI. Summary	94

I. INTRODUCTION

A volumetric method for the determination of alpha-, beta-, and gamma-cellulose was described in a previous article.[1] In this method the three cellulose fractions are separated in the usual manner, in that the alpha-cellulose is filtered from a mixture of the ground sample and sodium hydroxide solution, and the beta-cellulose is allowed to settle in the acidified filtrate before a portion of the gamma-cellulose is removed. The amount of cellulose in each fraction is determined by quantitative oxidation with dichromate. The small size of the test sample, 0.3 g, the elimination of the usual moisture and ash determinations, and various other simplifications resulted in a relatively rapid procedure. The method was shown to give results

[1] Herbert F. Launer, J. Research NBS 18, 333 (1937) RP979.

for alpha-cellulose which were practically identical with those obtained by a gravimetric procedure. The data presented were obtained for: soda, chemically refined sulfite and bleached sulfate pulps, also washed new and old rags, and new-rag paper containing 8 percent of clay. None of the samples contained sizing materials or more than 0.2 percent of resin, the values for which were determined using ethyl alcohol-hydrochloric acid [2] solution.

The purpose of the present article is to show that the method is applicable to samples containing rosin, glue, and starch sizes, inorganic fillers, large amounts of lignin, or natural resins in any amount.

The method of study was that previously employed. Each material was analyzed both volumetrically and gravimetrically for alpha-cellulose, using the gravimetric results as the standard for comparison.

II. ANALYTICAL PROCEDURE

In the gravimetric method a 2-g sample was employed. The proper corrections for moisture, ash, and filler materials, resin, glue, starch, or lignin were made upon both the ground sample and the alpha-cellulose, which was filtered through cloth on a 7.5-cm Büchner funnel.

The volumetric method was slightly changed. A small disk of 80-mesh copper or bronze screen was placed in the Gooch crucible. This greatly facilitated filtration, especially in the testing of papers made from old rags with high beta-cellulose content. The screen was allowed to remain in the 12 *M* sulfuric acid until adhering fibers were dissolved, but was removed before the dichromate solution was added. This procedure was found by blank experiments to introduce no detectable error.

Aside from the adoption of the screen as a permanent part of the volumetric method, no other changes in procedure were introduced for papers containing glue, starch, and rosin, for which corrections are applied in the calculations.

However, when a paper contains lignin or an oxidizable filler, as for example, zinc sulfide, it is a much more rapid process to eliminate these materials than to determine their percentage content and correct for them.

It was found that the effect of lignin upon the volumetric results could be satisfactorily eliminated by the following procedure. The separation of alpha-cellulose was carried out on newsprint, sample 7 in table 1, in the usual manner, after which the alpha-cellulose was thoroughly macerated in 50 ml of 12 *M* sulfuric acid and allowed to stand for 30 minutes with occasional stirring. The greater part of the lignin remained undissolved and was then removed by filtration through a Büchner funnel 7.5 cm in diameter provided with an 80-mesh copper screen supporting a layer of asbestos. Fifty milliliters more of 12 *M* acid was used for rinsing, after which dichromate was added and the determination was completed in the usual manner. The amount of lignin which dissolved in the acid had only a negligible

[2] Herbert F. Launer, *Simplified determination of resin in pulps and papers*, J. Research NBS 18, 227 (1937) RP973. RP973 also defines the terms "resin" and "rosin," as used in the present work.

effect upon the results and was in any event compensated by the small amount[3] of lignin in the beta-plus-gamma fraction. This is seen from a comparison with the gravimetric results (table 1), in which careful determinations of the lignin in the alpha-cellulose and in the ground sample had been made and corrections applied. The volumetric value for alpha-cellulose with the lignin not removed was 93.7 percent.

Of the usual filler materials, zinc sulfide presents by far the greatest difficulties in the analysis of papers. Nevertheless, the effect of zinc sulfide on the results could also be easily eliminated. Approximately one-third of the zinc sulfide present[4] enters the beta-plus-gamma portion as a suspension and must be removed. This was accomplished in sample 6 by carrying out the separation in the usual manner, except that the filtrate was received in a 100-ml beaker and the alpha-cellulose was rinsed with 20 instead of 35 ml of water. To remove the suspended zinc sulfide, the beta-plus-gamma portion was then filtered through a Gooch crucible, provided with a thick asbestos mat, directly into a 100-ml volumetric flask. The determination was carried out in the usual manner from this point. It was not found necessary to remove the filler from the alpha fraction. Results[5] obtained with other samples of paper with and without zinc sulfide indicated that the effect upon the gamma-cellulose values is negligible. In some analyses in which the zinc sulfide was not removed from the beta-plus-gamma portion the alpha-cellulose value was 78.7 percent, instead of 80.8 percent, as shown in table 1.

III. COMPARISON OF THE VOLUMETRIC AND GRAVIMETRIC RESULTS FOR ALPHA-CELLULOSE

The materials listed in table 1, column 1, together with those materials studied previously, represent a wide range of types encountered in paper chemistry.

A comparison of the alpha-cellulose values, obtained by each method, shows that entirely acceptable values for alpha-cellulose are obtained by the volumetric method. In calculating the results of the volumetric method, corrections for the sizing materials were made but the lignin and the inorganic fillers were neglected, because they had been essentially eliminated in the analytical procedure. The gravimetric results were in all cases corrected for these materials. The average deviation of the individual values from the means is 0.13 percent for the volumetric and 0.19 percent for the gravimetric results, which indicates somewhat better reproducibility in the case of the volumetric method.

[3] The amount of lignin which dissolved in the alkali was 2.7 percent, since it was found that of the 22.7 percent of lignin in the ground sample, 20.0 percent remained with the alpha-cellulose. For lignin determination, see Paper Trade J. 87, 61 (1928) and modification by Willets, Tech. Assn. Papers 15, 116 (1932).

[4] This was found to be the case upon analyzing the alpha-cellulose obtained by the gravimetric procedure and the ground sample for zinc sulfide by TAPPI tentative standard T438m-36.

[5] Not shown in table 1.

TABLE 1.—*Volumetric and gravimetric percentages of alpha-cellulose compared, and the percentages of gamma-cellulose*

Samples [a]	Paper stock	Sizing materials, etc.		Alpha-cellulose by volumetric method		Alpha-cellulose by gravimetric method		Gamma-cellulose
		Kind	Amount					
			Percent	*Percent*	*Percent* (mean)	*Percent*	*Percent* (mean)	*Percent*
1a	New-rag [b]	Resin	1.9	95.2 95.2 95.0	95.1	95.6 95.2 95.0	95.3	2.8 2.4 2.8
1b	do	Resin Glue	1.9 1.6	95.9 96.2 96.3	96.2	96.2 96.2 96.1	96.2	2.1 1.9 2.1
2a	Old-rag	Resin	1.0	82.9 82.8 82.9	82.9	83.2 83.2 83.2	83.2	1.8 1.8 1.9
2b	do	Resin Glue	1.0 5.9	88.3 88.4 87.9	88.2	88.5 88.3 87.6	88.1	2.5 2.6 2.5
2c	do	Resin Starch	1.0 2.6	85.4 85.3 85.3	85.3	84.8 84.8 85.2	84.9	1.6 1.7 1.6
2d	do	Resin Starch [c]	1.1 0.7	86.7 86.4 86.2	86.4	86.0 85.4 85.9	85.8	2.0 1.9 1.9
2e	do	Resin Starch [c] Glue	1.1 0.7 3.4	89.8 89.7 90.3	89.9	90.0 89.7 89.2	89.6	2.4 2.4 2.5
3	Sulfite pulp	Resin	0.7	82.9 82.8 82.6 82.8	82.8	82.0 81.9 82.1	82.0	12.7 12.5 12.7 12.5
4	Sulfite paper	Resin	2.5	79.4 79.2 79.4	79.3	78.6 78.4 78.4	78.5	13.9 ..... 14.2
5	Soda-sulfite (1:1) paper	Resin TiO_2 $BaSO_4$	1.1 3.2 6.6	72.4 72.3 71.9	72.2	71.3 72.3 71.7	71.8	7.3 7.1 7.1
6	Rag-sulfite (1:1) paper	ZnS	3.9	81.1 80.3 80.9	80.8	81.2 80.8 81.0	81.0	....
7	Newsprint	Resin, etc. [d] Lignin	1.2 22.7	91.7 91.7 91.5	91.6	92.4 92.6 92.6	92.5	8.3 8.3 8.5
8	Unbleached sulfate (kraft) paper.	Resin	1.0	85.2 85.0 84.9	85.0	85.4 84.7 85.8	85.3	14.8 15.0 15.1

[a] All papers bearing identical numbers were made from fibrous materials from the same sources; the letters indicate a difference in amount and kind of other materials present.

[b] The new-rag paper was made from No. 1 white shirt-cuttings. The old-rag paper was made from "twos and blues" and No. 1 old white rags in the proportion 1:1.

[c] This starch had been added in the beater, otherwise the glue and starch were surface sizes.

[d] In this instance, the resin content was determined using benzene-alcohol (2:1) solution, instead of ethyl alcohol-hydrochloric acid solution.

IV. CORRECTIONS FOR THE SIZING MATERIALS

In order to apply corrections for resin, glue, and starch, it is necessary to know the amounts of these materials in the various fractions and also the dichromate equivalent of each.

1. DICHROMATE EQUIVALENTS OF THE SIZING MATERIALS

The dichromate equivalents of resin, glue, and starch were determined as nearly as possible under test conditions. Small amounts of materials, corresponding to the quantities in 0.3-g samples, were weighed out and dissolved in water,[6] after which 50 ml of concentrated sulfuric acid, 2.50 ml of dichromate solution, corresponding to the amount which usually remains after oxidation of the beta-plus-gamma

[6] Saturated sodium carbonate solution was used to dissolve the rosin.

cellulose, and enough water to make a total volume of 100 ml, were added, and maintained at a temperature of 140 to 150° C for 10 minutes. The results are given in table 2.

TABLE 2.—*Dichromate equivalents for resin, glue, and starch*

Material	Weight taken	Dry weight	Volume of 1.835 *N* dichromate solution used	Dichromate equivalent. Grams of material per milliliter of 1.835 *N* dichromate solution
	g	g	ml	
Rosin (papermakers' grade *F*)	0.0066	0.0066	1.01	0.0065
	.0060	.0060	0.89	.0067
Average				0.0066
Glue [1]	0.0160	0.0139	0.91	0.0153
	.0165	.0144	.92	.0156
Average				0.0154
Starch	0.0160	0.0142	1.09	0.0130
	.0114	.0101	0.79	.0128
Average				0.0129

[1] The glue in the samples analyzed was a high-grade hide glue and was listed as No. 4 in table 1 of the publication, *Use of glue in coated paper*, by Hamill, Gottschalk, and Bicking, Tech. Pap. BS **20** (1926); T323. Other samples of glue, listed in the same table, were No. 1, a medium-grade hide glue; No. 3, a high-grade bone glue; and No. 6, a low-grade bone glue. These gave dichromate values of 0.0137, 0.0142, and 0.0140 g per ml respectively. The average of the four values is 0.0143, which, if used instead of 0.0154, would have caused a difference of 0.1 and 0.4 percent in the alpha cellulose percentages for samples 1b and 2b, respectively.

Precision higher than 2 to 3 percent should not be expected in such experiments, but it is interesting to note that the value for starch is in fair agreement with the theoretical value 0.0124, based upon the empirical formula $C_6H_{10}O_5$. The value for rosin, 0.0066, after dividing by 0.001 835, the number of oxidation equivalents in 1 ml of 1.835 *N* dichromate, gives an equivalent weight of 3.6, which is in good agreement with the value (3.63) obtained when using much larger quantities of rosin.[7]

2. DISTRIBUTION OF THE SIZING MATERIALS AMONG THE THREE CELLULOSE FRACTIONS AND THE METHOD OF APPLYING THE CORRECTIONS

(a) ALPHA FRACTION

For the purpose of determining the amounts of resin, glue, and starch in the alpha fraction, 5-g samples of each kind of paper listed in table 1 were treated with the usual proportions of sodium hydroxide solution and water. The alpha-cellulose was removed by filtration through an 80-mesh copper screen on a Büchner funnel, 7.5 cm in diameter, and analyzed for resin, glue, or starch.[8] The quantities remaining with the alpha-cellulose, based upon the oven-dry weight

[7] J. Research NBS **18**, 230 (1937) RP973. In this article it is also shown that the natural resins in soda and sulfite pulps have approximately the same equivalent weight and, therefore, the same dichromate equivalent as papermakers' rosin, grade *F*.

[8] Glue and starch were determined by use of TAPPI standards T418m (corrected May 15, 1935) and T420m (corrected March 15, 1934), respectively.

of the original sample, were found to be on the average as follows: Glue, 0.25 percent;[9] starch, 0.2 percent; and resin, 0.1 percent. The last value is applicable only when all the resin has been added in the form of rosin. In the case of natural resins, the amount remaining with the alpha-cellulose is 0.3 percent.

The manner of applying the corrections is illustrated by calculation of the alpha-cellulose content of sample 2e, table 1. The alpha-cellulose fraction, to which 25.00 ml of dichromate had been added, required after oxidation, 23.37 ml of ferrous ammonium sulfate, 1 ml of which solution was equivalent to 0.2485 ml of dichromate. The dichromate consumed was, therefore,

$$25.00-(23.37\times 0.2485)=19.19 \text{ ml.}$$

One-half of the beta-plus-gamma fraction, to which 5.00 ml of dichromate had been added, required after oxidation, 13.57 ml of ferrous ammonium sulfate. The dichromate consumed by the beta-plus-gamma fraction was, therefore,

$$2[5.00-(13.57\times 0.2485)]=3.26 \text{ ml.}$$

Rosin, glue, and starch were present in the beta-plus-gamma portion in the amounts of 1.0, 3.15, and 0.5 percent, respectively, which values were obtained by subtracting the amounts remaining with the alpha-cellulose from the values given in column 2 of table 1. From this, from the dry weight of the sample, 0.28 g, and from the corresponding factors given in table 2, column 5, the corrections in terms of dichromate solution are obtained as follows:

$$\text{For rosin: } \frac{0.28\times .01}{0.0066}=0.42 \text{ ml;}$$

$$\text{for glue: } \frac{0.28\times .0315}{0.0154}=0.57 \text{ ml; and}$$

$$\text{for starch: } \frac{0.28\times .005}{0.0129}=0.11 \text{ ml.}$$

The total correction is, therefore, 1.10 ml, and the corrected dichromate value for the beta-plus-gamma portion is 2.16 ml. After similar corrections, the corresponding value for the alpha portion is 19.06, and the alpha-cellulose content is

$$\frac{19.06}{19.06+2.16}\times 100=89.8 \text{ percent.}$$

(b) GAMMA FRACTION

The distribution of sizing materials among the beta and gamma fractions is best determined by comparing the gamma-cellulose values of a series of papers made from the same base paper but having variations in the kind and amount of sizing materials. On the assumption that the glue remains in solution with the gamma-cellulose

[9] Previous work at this Bureau gave values that were somewhat lower for glue. See Burton and Rasch, BS J. Research 6, 603 (1931) RP295. Those experiments were performed on alpha-cellulose from a gravimetric procedure, in which much larger amounts of wash water had been used. No results for starch were obtained.

and is oxidized, the latter was corrected for glue in paper 2b, table 1. The agreement with the gamma-cellulose value of paper 2a is fair, whereas, if the correction had not been made, the gamma-cellulose value would have been 7.6 percent, which obviously is too high. For starch, the same reasoning may be applied, for if the correction for the 2.4 percent of starch in the beta-plus-gamma portion of sample 2d were not applied, the gamma-cellulose value would be 4.1 percent, which obviously is too high, whereas, after making the correction, the value obtained is in good agreement with that of 2a. On the other hand, rosin would be expected to precipitate rather completely with the beta-cellulose, under the conditions of acidity specified in the method (approximately 0.4 *N* in H_2SO_4). This is indicated by the results for samples 1a and 1b, table 1, where, if the resin correction of 0.76 ml had been applied, the values for the gamma-cellulose would have become negative, since the correction would have been greater than the uncorrected dichromate value for the gamma portion. A large number of experiments, performed [10] in another connection, further substantiate this. On a series of papers made from a chemically refined sulfite pulp, and having resin contents of 0.2, 1.1, 1.6, 1.7, and 1.9 percent, the gamma-cellulose values, without applying corrections for resin, were 5.6, 5.4, 5.8, 7.0, and 6.6 percent, respectively. If corrections are applied, the values become low: 5.6,[11] 3.4, 2.9, 3.9, and 3.0 percent, respectively. Consequently, although some resin may occasionally enter the gamma portion, better results, on the whole, are obtained by neglecting it. Thus, the glue and starch but not the resin are corrected for in the gamma portion.

V. DICHROMATE EQUIVALENTS FOR CELLULOSE AND LIGNIN

By combining the gravimetric and volumetric data for any given pulp or paper, in this article and the preceding one, it is possible to calculate the cellulose-dichromate value. The results are given in table 3 for materials relatively free from pentosans.[12] The average value agrees well with the theoretical value 0.01239, the weight in grams of cellulose oxidized by 1 ml of 1.835 *N* dichromate solution, calculated on the basis of the chemical equation for the oxidation of cellulose by dichromate:

$$C_6H_{10}O_5+4Cr_2O_7^{--}+32H^+=6CO_2+21H_2O+8Cr^{+++}$$

This constitutes an additional substantiation of the various steps involved in the analyses.

[10] This work was done by C. I. Pope.

[11] No corrections are applicable to this particular value as natural resins to the extent of 0.3 percent or less remain with the alpha-cellulose, as previously explained.

[12] Pentosans present in the usual amounts do not affect the cellulose-dichromate value appreciably, however, since the pentosan-dichromate value, calculated on the basis of the formula for pentosans, $C_5H_8O_4$, is similar, 0.01212 g per milliliter of 1.835 *N* dichromate solution. This explains the fact that pentosans, no matter how they are distributed among the three cellulose fractions, do not seriously affect the results obtained by the volumetric method for alpha-cellulose. In a previous publication (see footnote 1) the pentosan-dichromate value was incorrectly calculated to be 0.0220, which necessitated the assumption that pentosans must be distributed among the three cellulose fractions in the same manner as cellulose itself, in order to explain the agreement between gravimetric and volumetric results for alpha-cellulose. There is, therefore, no longer a basis for this assumption.

TABLE 3.—*Dichromate equivalent for the cellulose in the various materials*

Sample	Material	Dichromate equivalent: Grams of cellulose per 1 ml of 1.835 *N* dichromate	Sample	Material	Dichromate equivalent: Grams of cellulose per 1 ml of 1.835 *N* dichromate
[1] 1009	No. 1 old white rags	0.01241	2a	Old-rag paper	.0122
1008	No. 1 new white rags	.01246	2b	Old-rag paper	.0124
988	Refined [2] sulfite pulp	.01246	2c	Old-rag paper	.0123
1a	New-rag paper	.01243	2d	Old-rag paper	.0124
1b	New-rag paper	.01248	2e	Old-rag paper	.0134
				Average	0.01242

[1] The first three materials are dealt with in the preceding article.
[2] Sulfite pulp which had been subjected to additional chemical purifying processes by the manufacturer.

It is of interest to calculate the dichromate value for lignin, using the following data for newsprint. The complete analysis of the newsprint, necessary in the gravimetric method for alpha-cellulose, permits the calculation of the amounts of materials in a 0.3-g sample.

	Grams
Moisture	0.0293
Ash	.0030
Resin, fats, etc	.0032
Lignin	.0614
Cellulose	.2030

A 0.300-g sample of newsprint consumed 23.55 ml of dichromate. Subtracting the resin correction, 0.49 ml, obtained as previously illustrated, and the cellulose "correction" .2030/.0124=16.37 ml from this, the volume of dichromate consumed by the lignin was 6.69 ml. This gives the lignin-dichromate value of 0.0092, which is in approximate agreement with the theoretical value 0.0072, based on the formula [13] $C_{43}H_{42}O_{14}$, and on the assumption of complete oxidation to CO_2. The value found is to be regarded as an upper limit, strictly speaking, but suffices to indicate that lignin is more oxidized than rosin but less so than cellulose or papermakers' glue and starch.

VI. SUMMARY

The main results of the present work and that described in the previous article are as follows:

1. A relatively rapid and simple method for the determination of alpha-, beta-, and gamma-cellulose in pulps and papers has been developed. A 0.3-g sample, which need not be weighed accurately, is employed. The separation of the alpha from the beta and gamma fractions is performed in a Gooch crucible provided with a disk of 80-mesh copper or bronze screen, which permits very rapid filtration for all types of materials.

2. The entire alpha fraction, and unusually large aliquot parts, one-half and one-fourth, of the filtrate are taken for the analysis of the beta-plus-gamma and the gamma fractions, respectively, thus minimizing the multiplication of errors. The amount of each cellulose fraction is determined volumetrically by oxidation with potassium

[13] From an article by Walter M. Fuchs, *The chemical nature of lignin*, Paper Trade J. 102, 33 (1936). The agreement with the theoretical value is not close enough to substantiate the formula given. It merely shows that the order of magnitude is correct.

dichromate solution, the strength of which need not be known accurately, as the concentrations of the oxidimetric solutions do not enter into the calculations.

3. By comparison with the results obtained by a gravimetric procedure, the method is shown to be applicable to a wide range of materials, including soda, sulfite, chemically refined sulfite, and bleached sulfate pulps, also new rags and old rags, and papers made from various pulps, pulp mixtures, rags, rag mixtures, and wood-pulp rag mixtures.

4. Corrections may be made for natural resins and rosin, glue, and starch in the alpha-and gamma-cellulose portions in a manner described in detail.

5. Neither moisture nor ash determinations are made on the alpha-cellulose or on the ground sample, in fact, no precision weighings are involved. This constitutes a saving of time in the analysis of papers containing clay, titanium dioxide, or barium sulfate, and is particularly advantageous when the fillers are either zinc sulfide, calcium carbonate, or calcium sulfite, which change upon ignition.

6. The analysis of pulps or papers containing large amounts of lignin is greatly simplified as no knowledge of the lignin content is necessary.

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